Supporting Information

Access to α-Carbonyl Vinyl Sulfoxonium Ylides via Tandem Arrangement-Addition of Cyclic Ethynylethylene Carbonates

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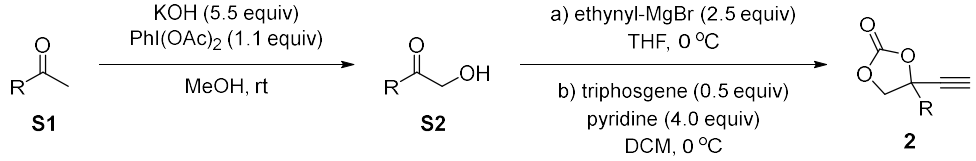
General information

Unless otherwise stated, all reactions were carried out in dry Schlenk tubes. Solvents were dried prior to use. Commercially obtained reagents were used as received. Reactions were monitored by analytical thin-layer chromatography (TLC) using pre-coated (0.20 mm thickness) silica gel plates with F254 indicator. Visualization of spots after TLC was accomplished by exposure to UV light (254 nm) and/or staining agents (iodine vapor, $KMnO_4$ in water). For column chromatography, 200-300 mesh silica gel was used. NMR spectra were recorded on a Bruker AVANCE III 400 MHz (400 MHz for ^1H NMR, 101 MHz for ^{13}C NMR) or 300 MHz (300 MHz for ^1H NMR, 75 MHz for ^{13}C NMR, 282 MHz for ^{19}F NMR) spectrometer using residual solvent peaks as the internal standard ($CDCl_3$: 7.26 ppm for ^1H NMR, 77.16 ppm for ^{13}C NMR; $(CD_3)_2SO$-d6: 2.50 ppm for ^1H NMR, 39.6 ppm for ^{13}C NMR). Data for ^1H NMR spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, m = multiplet), coupling constants J in Hertz (Hz), and integration. Data for ^{13}C NMR spectra were reported in terms of chemical shift (δ ppm). High resolution mass spectra (HRMS) were performed on Agilent 6540 Q-TOF or Agilent 6230A TOF mass spectrometer (ESI). GCMS was performed on Agilent Technologies 7820A (EI). Melting points were uncorrected and determined on a SGW X-4B melting point apparatus. The measurements of crystal were taken in a Bruker D8 Venture diffractometer. The data were integrated by Bruker D8 with multi-scan absorption corrections. The structure solution and refinement were processed by SHELXL (2018/3). All of the copper salts were commercially available and purchased from Energy Chemical, Titan Scientific, and Bidepharm.

Preparation of substrates

L1-L5[1a], **L6**[1b], **L7**[1c], **L4**[1d] were known compounds and prepared according to the literature procedures.[1] Compounds **1** and **4** were prepared according to the literature procedures.[2] The propargylic cyclic carbonate **2** was prepared according to literature procedures.[3] Compounds **6** were prepared according to the literature procedures.[4]

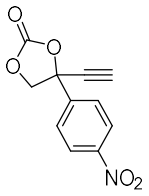
General procedure for the preparation of substrates 2



To a cold solution of ketone **S1** (15 mmol, 1.0 equiv) in MeOH was added KOH (4.629 g, 82.5 mmol, 5.5 equiv) in portions. Subsequently, $PhI(OAc)_2$ (diacetoxyiodobenzene) (5.314 g, 16.5 mmol, 1.1 equiv) was added slowly. The reaction mixture was stirred from 0 °C to room temperature for 2–3 h and then concentrated under reduced pressure. The residue was partitioned between H_2O (30 mL) and Et_2O (30 mL). The organic layer was separated, dried over Na_2SO_4 and filtered. The filtrate was concentrated, and the resulting residue was dissolved in MeOH (30 mL) and 2 N HCl (30 mL). The mixture was stirred overnight at room temperature. It was then carefully neutralized to pH = 7 with a saturated aqueous $NaHCO_3$ solution and diluted with DCM (30 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure, and the crude residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1) to afford **S2**.

A solution of hydroxy methyl ketone **S2** (5 mmol, 1.0 equiv) in THF (20 mL) was cooled to 0 °C. Ethynylmagnesium bromide (0.5 M in THF, 2.5 equiv) was added, and the reaction was stirred under an argon atmosphere at room temperature for 2 h. The mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to afford the crude product, which was used directly in the next step without further purification.

To a solution of the corresponding crude diol (1.0 equiv) and pyridine (4.0 equiv) in DCM (20 mL) was added triphosgene (0.5 equiv) at 0 °C. The reaction was stirred under an argon atmosphere at room temperature for 2 h. The reaction mixture was then quenched with saturated aqueous NH_4Cl, and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1) to afford the corresponding propargylic cyclic carbonate **2**.



4-Ethynyl-4-(4-nitrophenyl)-1,3-dioxolan-2-one (2e)

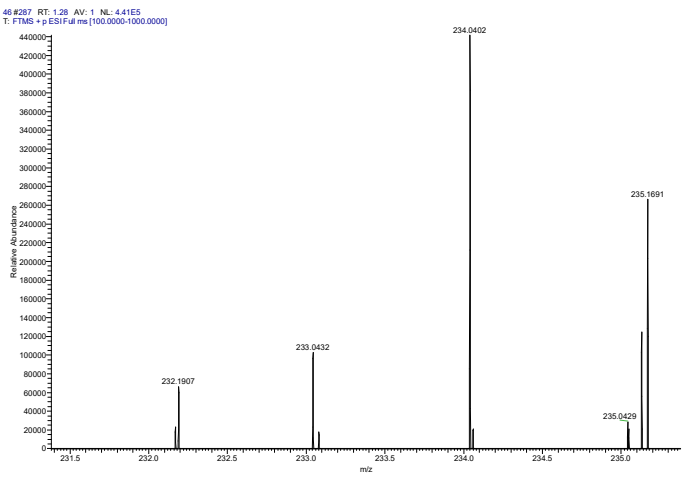
According to the general procedure for preparing cyclic carbonate **2**, obtained as a brown solid (957 mg, 82%), mp: 93.9-95.9 °C.

R_f (petroleum ether/ethyl acetate = 3:1) = 0.5.

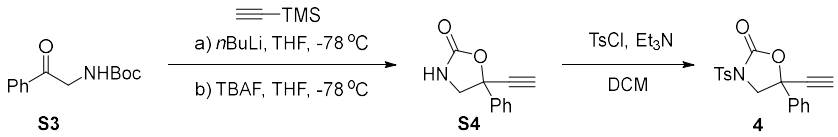
^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 9.0 Hz, 2H), 7.79 (d, *J* = 9.0 Hz, 2H), 4.89 (d, *J* = 8.6 Hz, 1H), 4.50 (d, *J* = 8.6 Hz, 1H), 3.10 (s, 1H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 152.8, 148.7, 143.3, 126.3, 124.4, 79.8, 78.8, 78.0, 76.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_8NO_5$ 234.0397; Found 234.0402.



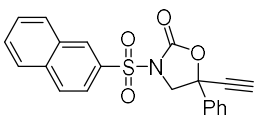
General procedure of Ethynyl Oxazolidinones



Ethynyl oxazolidinones were prepared according to the methods reported in the literature with some modifications. Trimethylsilylacetylene (2.95 g, 30 mmol) was dissolved into 50 mL THF and cooled to 0 °C, then *n*-BuLi (30 mmol, 2.5 M in Hexane, 12 mL) was added and stirred at this temperature for 1 h under argon atmosphere. The mixture was then cooled to -78 °C, and tert-butyl (2-oxo-2-phenylethyl) carbamate **S3** (10 mmol) in 10 mL THF was added. The mixture was allowed to stir at this temperature for further 10 min before warmed to room temperature and stirred overnight. A saturated solution of NH_4Cl (20 mL) was added and the aqueous phase was extracted with EtOAc. The combined extracts were dried by Na_2SO_4 and the solvent removed under vacuum. The crude product was used directly in the next step without further purification.

The crude product was dissolved in THF (30 mL) and cooled to -78 °C. TBAF (1.0 M in THF, 10 mL) was added and stirred 1 h at this temperature before quenching with saturated solution of NH_4Cl (10 mL). The mixture was extracted with EtOAc, and the organic mixture was dried by Na_2SO_4 and concentrated under reduced pressure. The concentrate was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 2:1) to give the product **S4** as a white solid.

The ethynyl oxazolidinones (374 mg, 2.0 mmol, 1.0 equiv) and Et_3N (405 mg, 4.0 mmol, 2.0 equiv) were dissolved in DCM (5 mL). The mixture was then cooled to 0 °C, and TsCl (570 mg, 3.0 mmol, 1.5 equiv) was added dropwise. The mixture was warmed to room temperature and stirred for 8 h before quenching with saturated solution of NH_4Cl (5 mL). The mixture was extracted with DCM. The organic mixture was dried by Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 2:1) to give the cyclic ethynylethylene carbamates **4**.



5-Ethynyl-3-(naphthalen-2-ylsulfonyl)-5-phenyloxazolidin-2-one (4d)

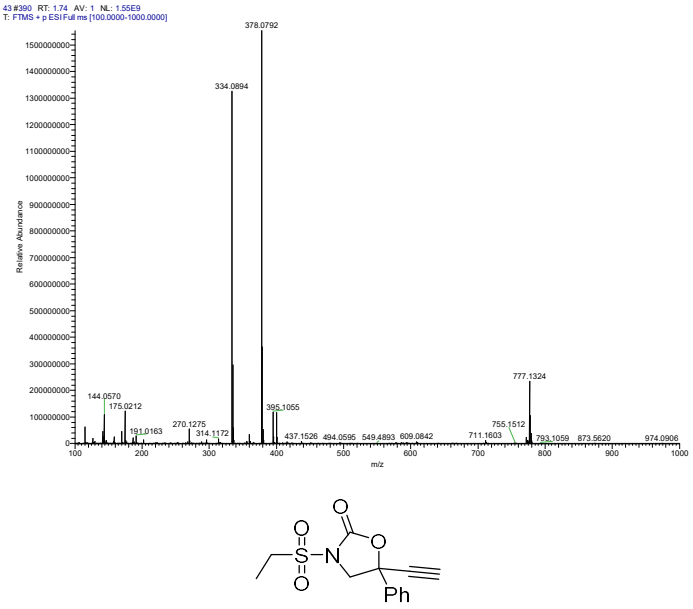
According to the general procedure for preparing ethynyl oxazolidinones, obtained a colorless oil (528 mg, 70%).

R_f (petroleum ether/ethyl acetate = 3:1) = 0.5.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.63 (s, 1H), 8.01 – 7.98 (m, 3H), 7.95 – 7.88 (m, 1H), 7.71 – 7.60 (m, 2H), 7.46 – 7.43 (m, 2H), 7.38 – 7.32 (m, 3H), 4.56 (d, *J* = 9.5 Hz, 1H), 4.19 (d, *J* = 9.5 Hz, 1H), 2.84 (s, 1H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 150.4, 137.1, 135.7, 133.6, 131.9, 130.6, 129.9, 129.82, 129.75, 129.1 128.04, 127.99, 125.0, 122.4, 80.2, 78.1, 76.4, 58.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{16}NO_4S$ 378.0795; Found 378.0792.



3-(Ethylsulfonyl)-5-ethynyl-5-phenyloxazolidin-2-one (4e)

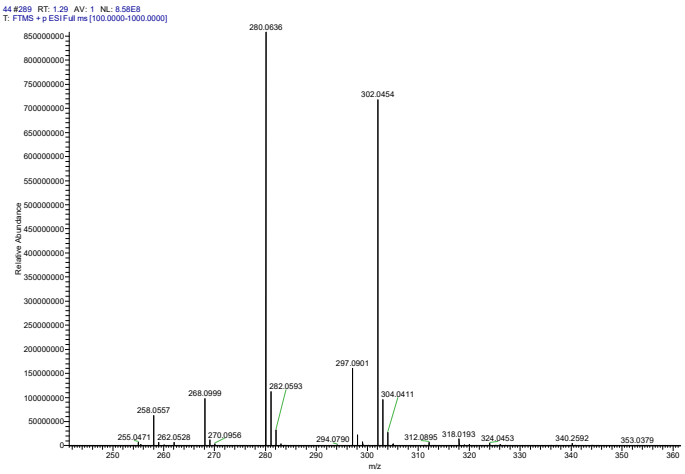
According to the general procedure for preparing ethynyl oxazolidinones, obtained a white solid (395 mg, 72%), mp: 117.4-119.4 °C.

R_f (petroleum ether/ethyl acetate = 2:1) = 0.4.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.54 (m, 2H), 7.49 – 7.43 (m, 3H), 4.46 (d, *J* = 9.6 Hz, 1H), 4.18 (d, *J* = 9.6 Hz, 1H), 3.68 – 3.48 (m, 2H), 2.97 (s, 1H), 1.45 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.2, 136.9, 129.9, 129.2, 125.0, 80.3, 78.1, 77.0, 58.3, 47.8, 7.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}NO_4S$ 280.0638; Found 280.0636.



3-(Butylsulfonyl)-5-ethynyl-5-phenyloxazolidin-2-one (4f)

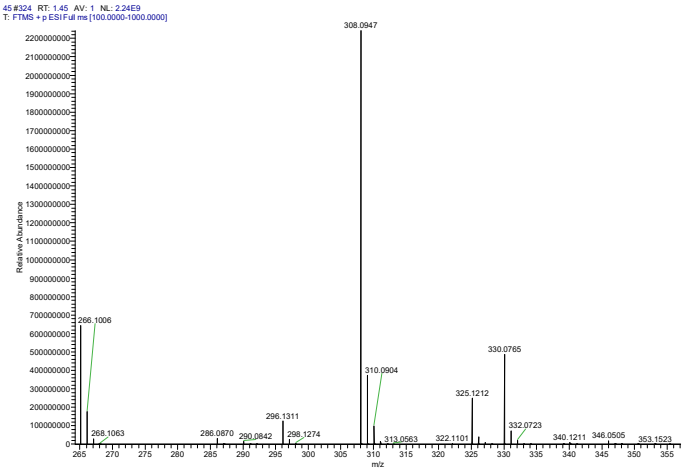
According to the general procedure for preparing ethynyl oxazolidinones, obtained a colorless oil (464.6 mg, 76%).

R_f (petroleum ether/ethyl acetate = 5:1) = 0.5.

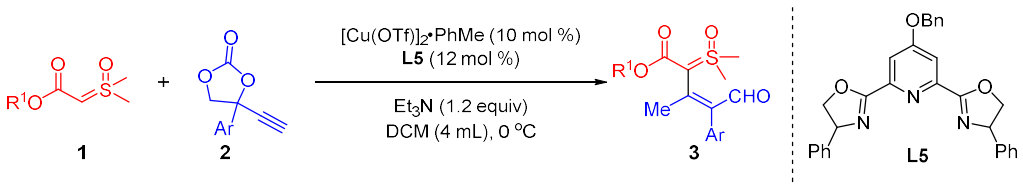
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.34 (m, 2H), 7.28 – 7.21 (m, 3H), 4.26 (d, *J* = 9.6 Hz, 1H), 3.97 (d, *J* = 9.6 Hz, 1H), 3.41 – 3.26 (m, 2H), 2.79 (s, 1H), 1.70 – 1.56 (m, 2H), 1.28 (h, *J* = 7.4 Hz, 2H), 0.75 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.3, 137.0, 129.9, 129.2, 125.0, 80.3, 78.2, 76.9, 58.2, 52.9, 24.9, 21.3, 13.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}NO_4S$ 308.0951; Found 308.0947.

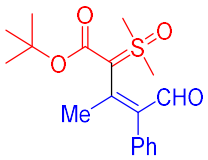


General Procedure for the Synthesis of Compounds 3



To a dry Schlenk tube were added $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4

mg, 0.024 mmol, 12 mol%) and dry DCM (1.0 mL). The resulting mixture was stirred at room temperature for 0.5 h. Then **1** (0.2 mmol, 1.0 equiv), **2** (0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) and dry DCM (3.0 mL) were added sequentially to the above solution at room temperature. The resulting mixture was stirred at 0 °C for 16 h. The reaction mixture was concentrated under vacuum; the crude residue was purified by silica gel column chromatography to give **3**.



tert-Butyl (Z)-2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-3-methyl-5-oxo-4-phenylpent-3-enoate (3aa)

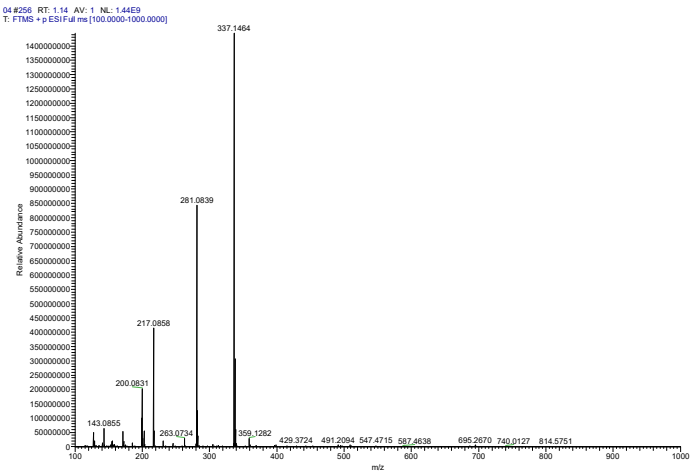
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), *tert*-butyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow oil (62.5 mg, 93%).

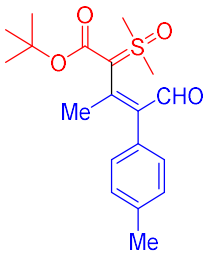
R_f (petroleum ether/ethyl acetate = 1:2) = 0.6.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.92 (s, 1H), 7.40 – 7.35 (m, 2H), 7.32 – 7.28 (m, 1H), 7.13 – 7.10 (m, 2H), 3.52 (s, 3H), 3.50 (s, 3H), 2.02 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.5, 165.5, 149.4, 143.1, 136.4, 129.9, 128.2, 127.3, 79.8, 68.2, 44.0, 43.7, 28.7, 24.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}O_4S$ 337.1468; Found 337.1464.





tert-Butyl (Z)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxo-4-(p-tolyl)pent-3-enoate (3ab)

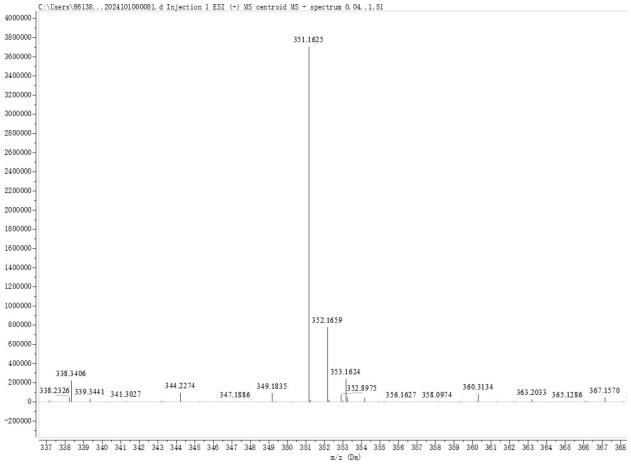
Prepared according to general procedure from [(CuOTf)]$_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), *tert*-butyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-(p-tolyl)-1,3-dioxolan-2-one (121.2 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow solid (58.4 mg, 82%). mp: 166.9-168.8 °C.

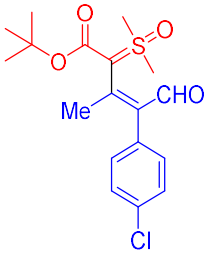
R$_f$ (petroleum ether/ethyl acetate = 1:2) = 0.5.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.92 (s, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 3.52 (s, 3H), 3.49 (s, 3H), 2.35 (s, 3H), 2.01 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.7, 165.6, 149.0, 143.2, 136.9, 133.3, 129.7, 128.9, 79.8, 67.9, 44.1, 43.8, 28.8, 24.7, 21.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}O_4S$ 351.1625; Found 351.1625.





tert-Butyl (Z)-4-(4-chlorophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxopent-3-enoate (3ac)

Prepared according to general procedure from[(CuOTf)]$_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5**

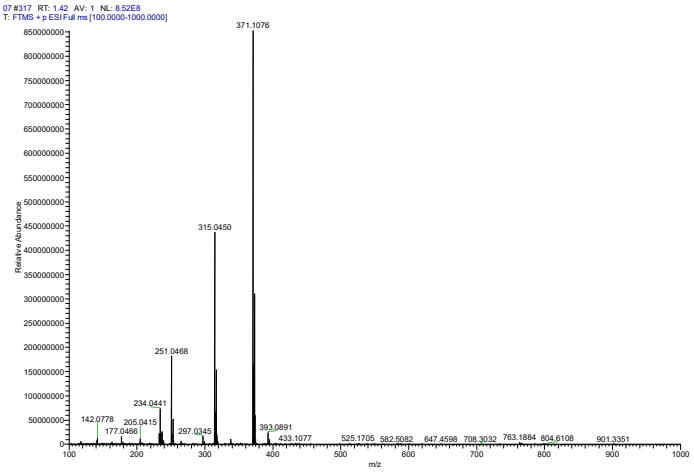
(11.4 mg, 0.024 mmol, 12 mol%), *tert*-butyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 4-(4-chlorophenyl)-4-ethynyl-1,3-dioxolan-2-one (133.2 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow solid (47.9 mg, 65%), mp: 157.9-159.9 °C.

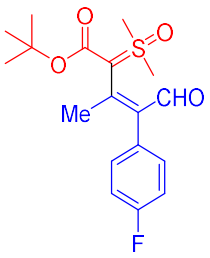
R_f (petroleum ether/ethyl acetate = 1:2) = 0.5.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.85 (s, 1H), 7.36 – 7.32 (m, 2H), 7.08 – 7.04 (m, 2H), 3.53 (s, 3H), 3.50 (s, 3H), 2.02 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.0, 165.5, 149.6, 141.6, 134.9, 133.1, 131.4, 128.4, 80.0, 67.9, 44.2, 44.0, 28.7, 24.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}ClO_4S$ 371.1078; Found 371.1076.





***tert*-Butyl (Z)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-(4-fluorophenyl)-3-methyl-5-oxopent-3-enoate (3ad)**

Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), *tert*-butyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-(4-fluorophenyl)-1,3-dioxolan-2-one (123.6 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow solid (57.8 mg, 82%), mp: 190.2-191.8 °C.

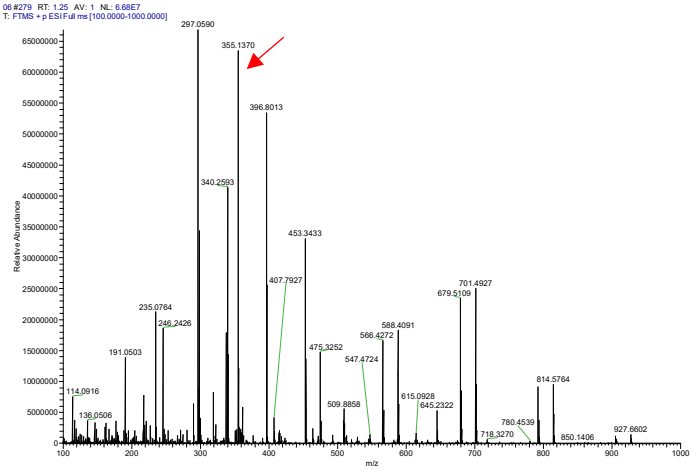
R_f (petroleum ether/ethyl acetate = 1:2) = 0.45.

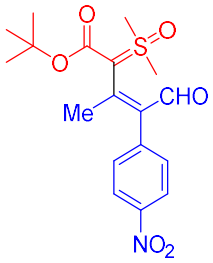
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.89 (s, 1H), 7.09 – 7.04 (m, 4H), 3.53 (s,3H), 3.51 (s, 3H), 2.02 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.2, 165.6, 162.1 (d, *J* = 245.8 Hz), 149.4, 142.0, 133.0 (d, *J* = 7.9 Hz), 131.6 (d, *J* = 8.0 Hz), 115.2 (d, *J* = 21.4 Hz), 79.9, 67.6, 44.3, 44.0, 28.7, 24.6.

^{19}F NMR (282 MHz, Chloroform-*d*) δ -115.24.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}FO_4S$ 355.1374; Found 355.1370.





tert-Butyl (Z)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-4-(4-nitrophenyl)-5-oxopent-3-enoate (3ae)

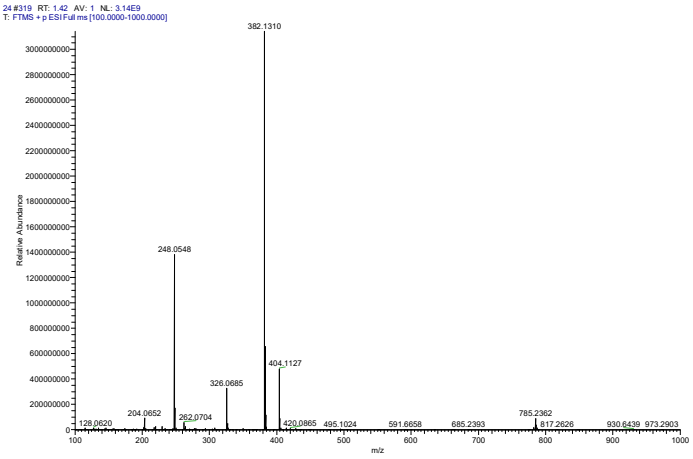
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), *tert*-butyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-(4-nitrophenyl)-1,3-dioxolan-2-one (139.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow solid (38.6 mg, 51%), mp: 159.9-161.7 °C.

R_f (petroleum ether/ethyl acetate = 1:2) = 0.3.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.82 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 3.57 (s, 6H), 2.05 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.0, 165.5, 150.2, 146.9, 144.0, 140.2, 131.2, 123.4, 80.4, 68.2, 44.6, 44.3, 28.7, 24.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}NO_6S$ 382.1319; Found 382.1310.



tert-Butyl (Z)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxo-4-(m-tolyl)pent-3-enoate (3af)

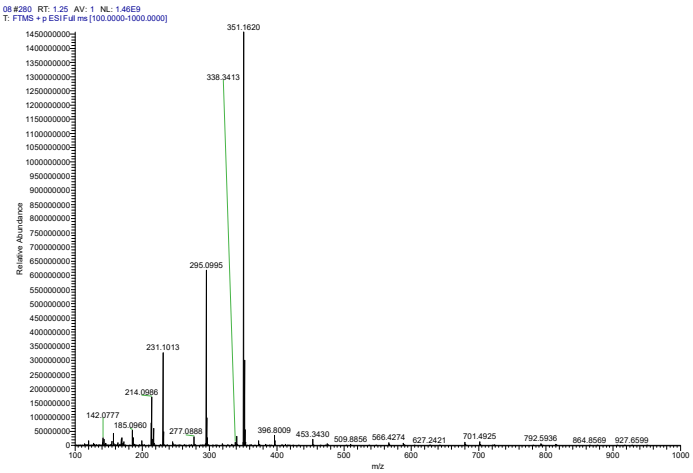
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), *tert*-butyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-(m-tolyl)-1,3-dioxolan-2-one (121.2 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow oil (59.3 mg, 85%).

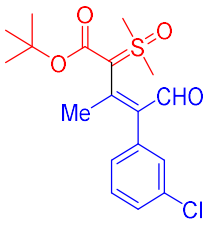
R_f (petroleum ether/ethyl acetate = 1:2) = 0.5.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.90 (s, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.95 – 6.86 (m, 2H), 3.51 (s, 3H), 3.47 (s, 3H), 2.35 (s, 3H), 2.01 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.7, 165.5, 149.3, 143.3, 137.7, 136.4, 130.5, 128.1, 127.9, 126.9, 79.8, 68.2, 44.0, 43.7, 28.8, 24.7, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}O_4S$ 351.1625; Found 351.1620.





tert-Butyl (Z)-4-(3-chlorophenyl)-2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-3-methyl-5-oxopent-3-enoate (3ag)

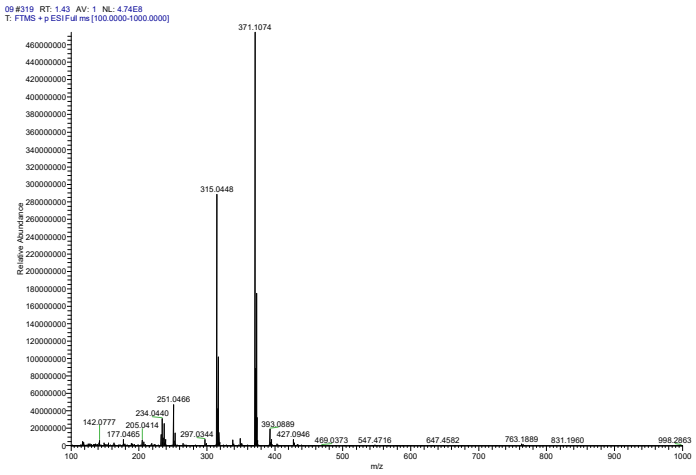
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), *tert*-butyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 4-(3-chlorophenyl)-4-ethynyl-1,3-dioxolan-2-one (133.2 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow solid (41 mg, 55%), mp: 159.8-161.8 °C.

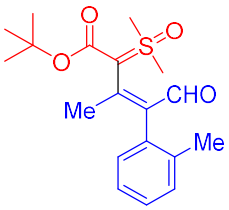
R_f (petroleum ether/ethyl acetate = 1:2) = 0.5.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.84 (s, 1H), 7.33 – 7.28 (m, 2H), 7.12 – 7.11 (m, 1H), 7.02 – 7.00 (m, 1H), 3.53 (s, 3H), 3.51 (s, 3H), 2.02 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.8, 165.5, 149.9, 141.4, 138.4, 133.9, 130.0, 129.5, 128.3, 127.4, 80.1, 68.1, 44.2, 44.0, 28.7, 24.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}ClO_4S$ 371.1078; Found 371.1074.





tert-Butyl (Z)-2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-3-methyl-5-oxo-4-(o-tolyl)pent-3-enoate (3ah)

Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), *tert*-butyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)acetate (38.4 mg,

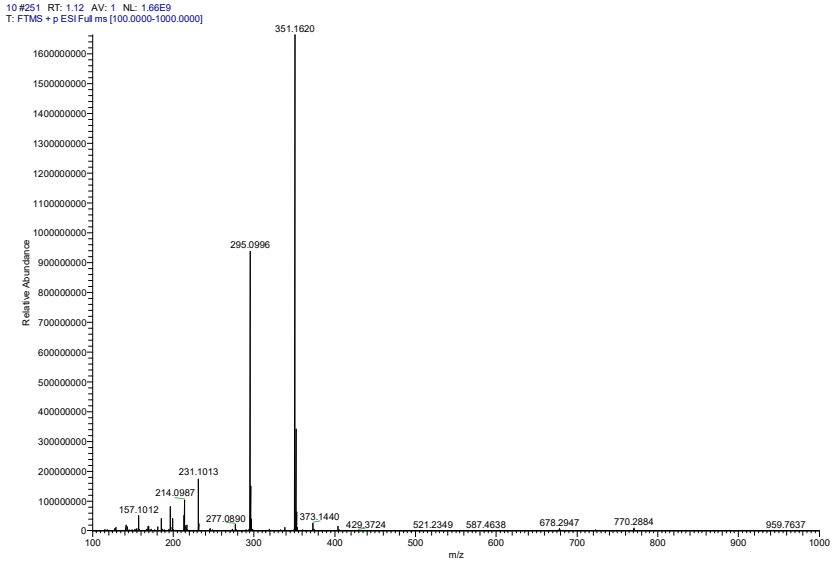
0.2 mmol, 1.0 equiv), 4-ethynyl-4-(o-tolyl)-1,3-dioxolan-2-one (121.2 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at RT for 12 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow solid (53.2 mg, 76%), mp: 181.8-183.8 °C.

R_f (petroleum ether/ethyl acetate = 1:2) = 0.5.

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.84 (s, 1H), 7.25 – 7.14 (m, 3H), 6.99 – 6.79 (m, 1H), 3.68 (s, 3H), 3.58 (s, 3H), 2.06 (s, 3H), 1.80 (s, 3H), 1.40 (s, 9H).

^{13}C NMR (75 MHz, DMSO-d_6) δ 191.9, 164.9, 151.4, 142.8, 137.2, 136.6, 130.0, 127.7, 126.0, 78.6, 70.4, 42.9, 42.3, 29.0, 25.0, 19.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}O_4S$ 351.1625; Found 351.1620.



***tert*-Butyl (Z)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-(2-fluorophenyl)-3-methyl-5-oxopent-3-enoate (3ai)**

Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), *tert*-butyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-(2-fluorophenyl)-1,3-dioxolan-2-one (123.6 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at RT for 12 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow solid (52.9 mg, 75%), mp: 191.2-193.1 °C.

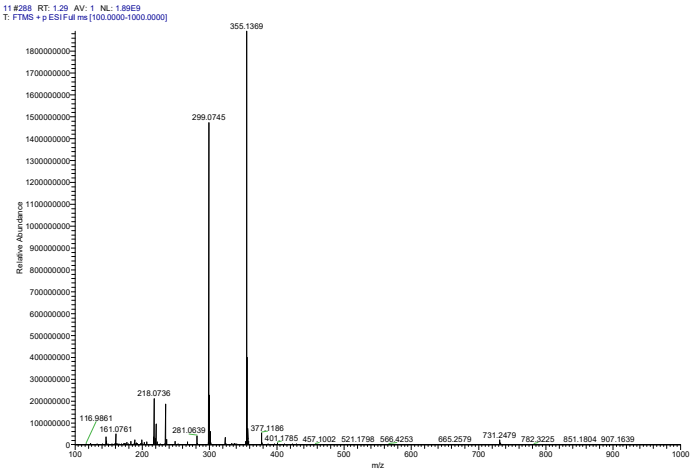
R_f (petroleum ether/ethyl acetate = 1:2) = 0.5.

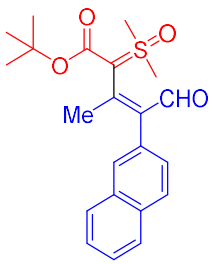
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.90 (s, 1H), 7.32 – 7.28 (m, 1H), 7.18 – 7.14 (m, 1H), 7.13 – 7.11 (m, 1H), 7.10 – 7.06 (m, 1H), 3.58 (s, 3H), 3.46 (s, 3H), 2.02 (s, 3H), 1.47 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.8, 165.3, 161.1, 158.7, 136.9, 132.1 (d, *J* = 3.9 Hz), 129.5 (d, *J* = 8.2 Hz), 124.0 (d, *J* = 3.4 Hz), 123.8 (d, *J* = 17.1 Hz), 115.5 (d, *J* = 22.0 Hz), 80.0, 44.1, 43.3, 28.7, 24.5 (d, *J* = 1.8 Hz).

^{19}F NMR (282 MHz, Chloroform-*d*) δ -113.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{24}FO_4S$ 355.1374; Found 355.1369.





***tert*-Butyl (Z)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-4-(naphthalen-2-yl)-5-oxopent-3-enoate (3aj)**

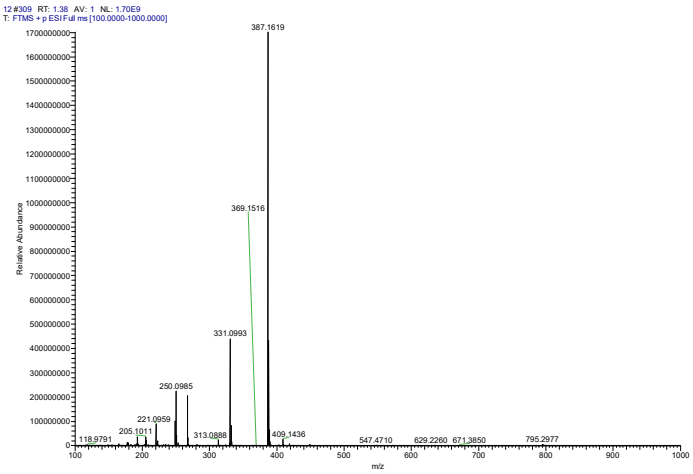
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), *tert*-butyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-(naphthalen-2-yl)-1,3-dioxolan-2-one (142.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow solid (64.4 mg, 85%), mp: 173.1-174.9 °C.

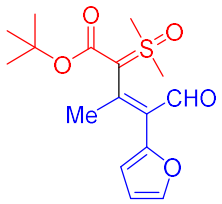
R_f (petroleum ether/ethyl acetate = 1:2) = 0.5.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.95 (s, 1H), 7.85 – 7.80 (m, 3H), 7.60 (s, 1H), 7.48 – 7.44 (m, 2H), 7.27 – 7.21 (m, 1H), 3.50 (s, 3H), 3.47 (s, 3H), 2.05 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.6, 165.6, 149.8, 142.9, 134.1, 133.3, 132.6, 130.2, 128.9, 128.1, 128.0, 127.7, 127.1, 125.9, 79.9, 68.3, 44.1, 43.8, 28.8, 24.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}O_4S$ 387.1625; Found 387.1619.





tert-Butyl (Z)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-(furan-2-yl)-3-methyl-5-oxopent-3-enoate(3ak)

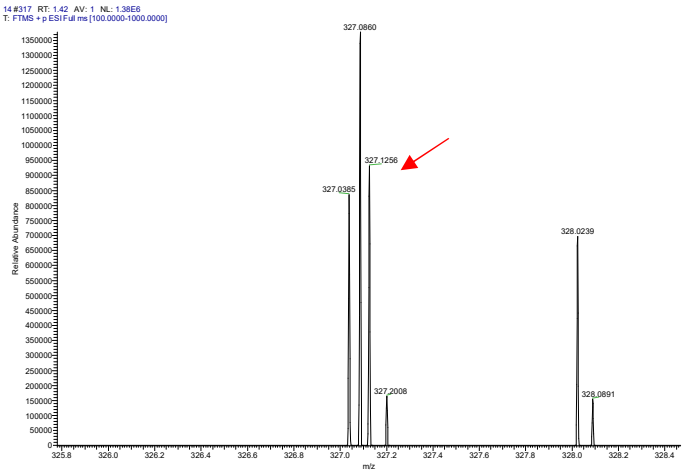
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), *tert*-butyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-(furan-2-yl)-1,3-dioxolan-2-one (106.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow oil (30.3 mg, 46%).

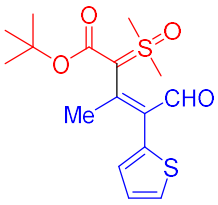
R_f (petroleum ether/ethyl acetate = 1:2) = 0.6.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.73 (s, 1H), 7.45 (s, 1H), 6.61 (d, *J* = 3.3 Hz, 1H), 6.49 – 6.43 (m, 1H), 3.56 (s, 3H), 3.45 (s, 3H), 2.31 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.6, 165.3, 150.5, 149.3, 141.7, 131.4, 111.3, 111.0, 80.3, 71.9, 44.0, 43.8, 28.7, 24.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{23}O_5S$ 327.1261; Found 327.1256.





tert-Butyl (E)-2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-3-methyl-5-oxo-4-(thiophen-2-yl)pent-3-enoate (3al)

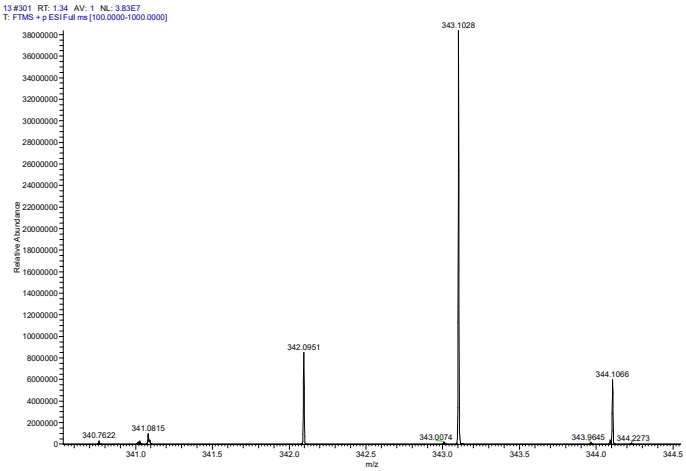
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), *tert*-butyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-(thiophen-2-yl)-1,3-dioxolan-2-one (116.4 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow solid (49.2 mg, 72%), mp: 137.3-139.3 °C.

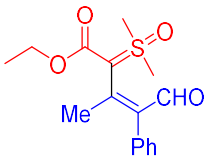
R_f (petroleum ether/ethyl acetate = 1:2) = 0.5.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.84 (s, 1H), 7.37 (d, *J* = 5.1 Hz, 1H), 7.08 – 7.05 (m, 1H), 6.94 (d, *J* = 3.5 Hz, 1H), 3.55 (s,3H), 3.49 (s, 3H), 2.23 (s, 3H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.4, 165.3, 151.3, 136.3, 135.1, 128.1, 126.6, 126.2, 80.2, 70.0, 44.2, 43.8, 28.7, 24.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{23}O_4S_2$ 343.1032; Found 343.1028.





Ethyl (Z)-2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-3-methyl-5-oxo-4-phenylpent-3-enoate (3ba)

Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), ethyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)acetate (32.8 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and

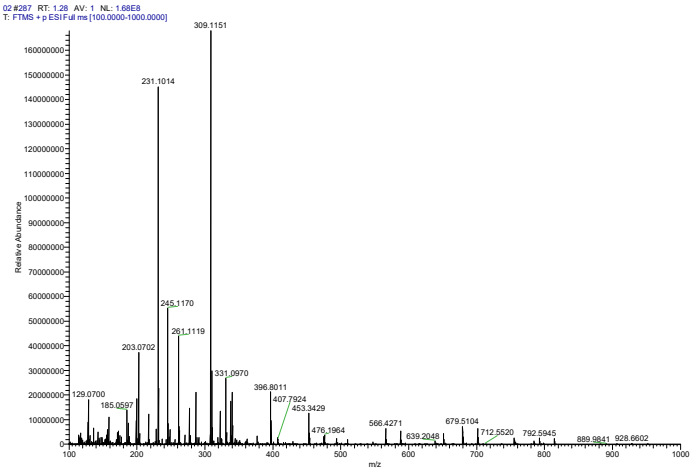
obtained as a yellow oil (48.6 mg, 79%).

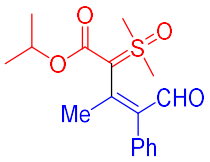
R_f (petroleum ether/ethyl acetate = 1:2) = 0.3.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.91 (s, 1H), 7.39 -7.35 (m, 2H), 7.31 - 7.29 (m, 1H), 7.14 - 7.11(m, 2H), 4.18 – 4.09 (m, 2H), 3.52 (s, 3H), 3.48 (s, 3H), 2.04 (s, 3H), 1.25 (td, *J* = 7.1, 1.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 191.4, 165.6, 148.5, 143.6, 136.3, 129.9, 128.2, 127.4, 67.2, 59.4, 43.7, 24.6, 14.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{21}O_4S$ 309.1155; Found 309.1151.





Isopropyl (Z)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxo-4-phenylpent-3-enoate (3ca)

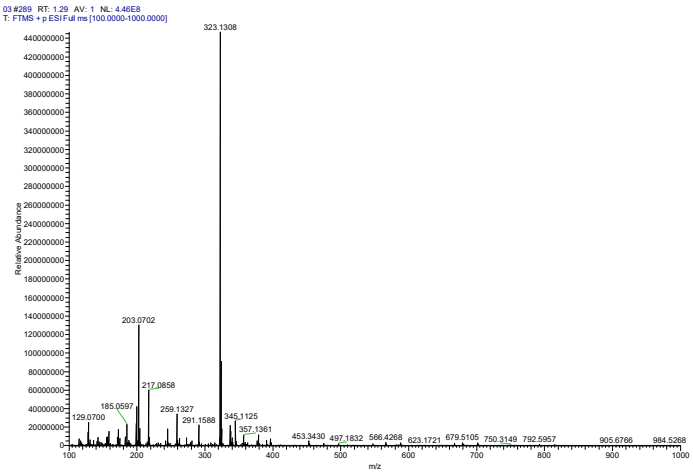
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), isopropyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (35.6 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow oil (61.0 mg, 95%).

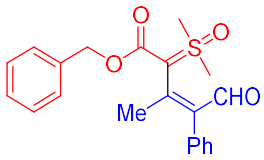
R_f (ethyl acetate) = 0.7.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.90 (s, 1H), 7.40 – 7.35 (m, 2H), 7.32 – 7.29 (m, 1H), 7.15 – 7.11 (m, 2H), 5.03 – 4.96 (m, 1H), 3.53 (s, 3H), 3.50 (s, 3H), 2.03 (s, 3H), 1.23 (d, *J* = 6.4 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.4, 165.3, 148.7, 143.6, 136.3, 129.9, 128.2, 127.3, 67.2, 66.8, 43.9, 24.6, 22.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}O_4S$ 323.1312; Found 323.1308.





Benzyl (Z)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxo-4-phenylpent-3-enoate (3da)

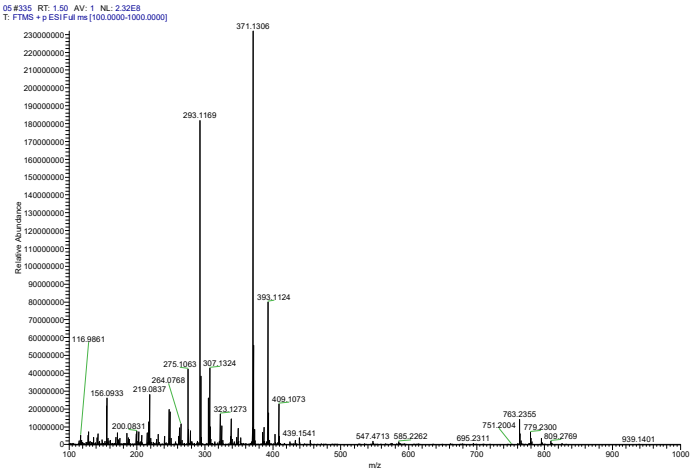
Prepared according to general procedure from [(CuOTf)]$_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), benzyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (45.2 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and obtained as a yellow oil (62.8 mg, 85%).

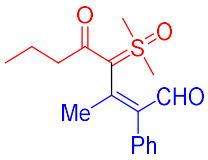
R$_f$ (ethyl acetate) = 0.7.

^{1}H NMR (300 MHz, DMSO-d_6) δ 9.88 (s, 1H), 7.39 – 7.27 (m, 8H), 7.08 – 7.05 (m, 2H), 5.12 – 5.07 (m, 2H), 3.72 (s, 3H), 3.60 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.5, 165.1, 148.4, 144.1, 136.9, 136.1, 131.3, 129.9, 128.5, 128.2, 127.9, 127.7, 127.4, 65.3, 43.6, 24.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}O_4S$ 371.1312; Found 371.1306.





(Z)-4-(Dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxo-2-phenyloct-2-enal (3ea)

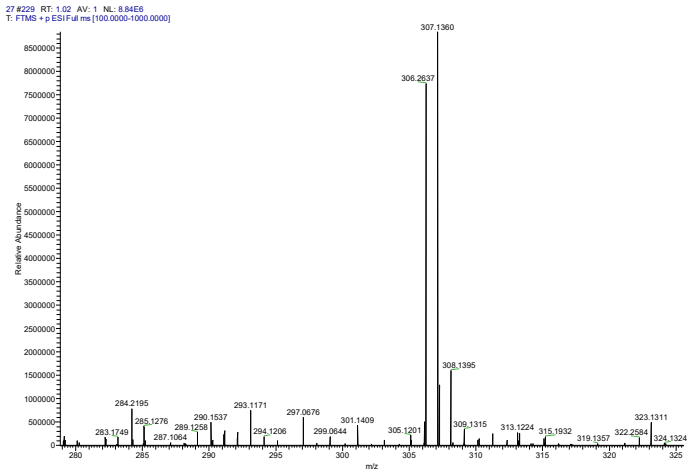
Prepared according to general procedure from [(CuOTf)]$_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), 1-(dimethyl(oxo)-λ^6-sulfaneylidene)pentan-2-one (32.4 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1-1:5) and obtained as a yellow oil (50.8 mg, 83%).

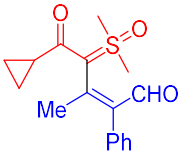
R$_f$ (ethyl acetate) = 0.4.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.89 (s, 1H), 7.42 – 7.38 (m, 2H), 7.35 – 7.30 (m, 1H), 7.10 – 7.08 (m, 2H), 3.68 (s, 3H), 3.65 (s, 3H), 2.23 – 2.16 (m, 1H), 2.10 – 1.99 (m, 1H), 1.98 (s, 3H), 1.50 (qd, J = 7.4, 2.6 Hz, 2H), 0.83 (t, J = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 192.2, 187.1, 151.3, 144.9, 136.5, 130.1, 128.6, 127.7, 85.5, 42.4, 41.9, 39.6, 26.1, 19.0, 14.3.

HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{17}H_{23}O_3S$ 307.1362; Found 307.1360.





(Z)-5-Cyclopropyl-4-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxo-2-phenylpent-2-enal (3fa)

Prepared according to general procedure from [(CuOTf)]$_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), 1-cyclopropyl-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan-1-one (32.0 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1-1:5)

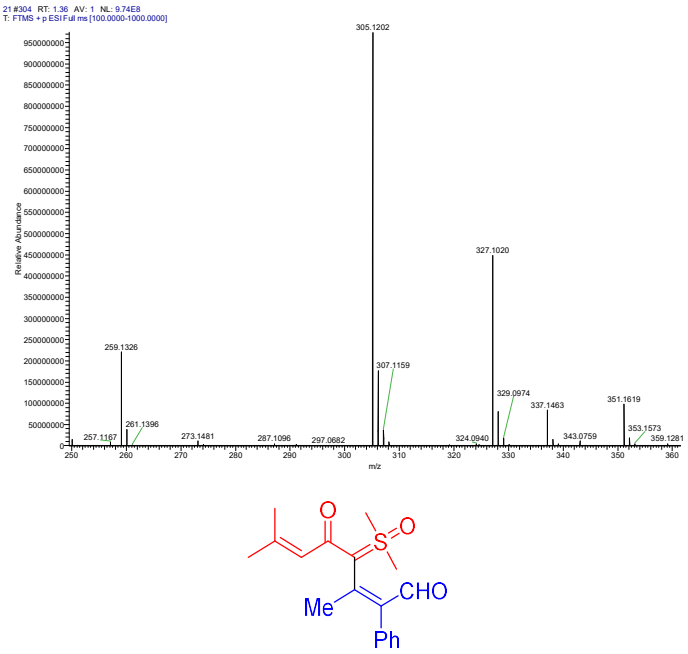
and obtained as a yellow oil (43.3 mg, 71%).

R_f (ethyl acetate) = 0.5.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.04 (s, 1H), 7.42 – 7.38 (m, 2H), 7.35 – 7.32 (m, 1H), 7.17 – 7.14 (m, 2H), 3.57 (s, 3H), 3.56 (s, 3H), 2.14 (s, 3H), 1.89 – 1.85 (m, 1H), 1.07 – 1.01 (m, 1H), 0.91 – 0.85 (m, 1H), 0.78 – 0.72 (m, 1H), 0.71 – 0.65 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.6, 188.3, 149.7, 145.6, 135.7, 129.7, 128.3, 127.6, 82.7, 43.8, 43.6, 25.9, 16.9, 8.8, 8.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}O_3S$ 305.1206; Found 305.1202.



(Z)-4-(Dimethyl(oxo)-λ^6-sulfaneylidene)-3,7-dimethyl-5-oxo-2-phenylocta-2,6-dienal (3ga)

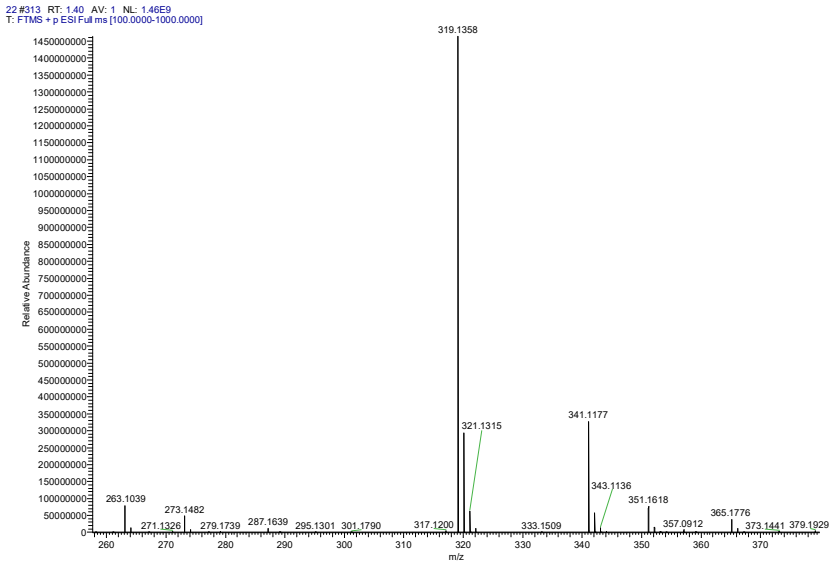
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-methylpent-3-en-2-one (34.8 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1-1:5) and obtained as a yellow solid (40.1 mg, 63%), mp: 194.7-196.7 °C.

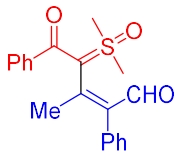
R_f (ethyl acetate) = 0.3.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.88 (s, 1H), 7.42 – 7.38 (m, 2H), 7.35 – 7.32 (m, 1H), 7.15 – 7.11 (m, 2H), 5.90 – 5.88 (m, 1H), 3.63 (s, 3H), 3.62 (s, 3H), 2.09 (d, J = 1.6 Hz, 3H), 2.05 (s, 3H), 1.80 (d, J = 1.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.1, 182.5, 149.4, 148.7, 145.5, 135.9, 129.7, 128.3, 127.6, 122.9, 84.9, 44.1, 43.5, 27.4, 25.5, 20.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{23}O_3S$ 319.1362; Found 319.1358.





(Z)-4-(Dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxo-2,5-diphenylpent-2-enal (3ha)

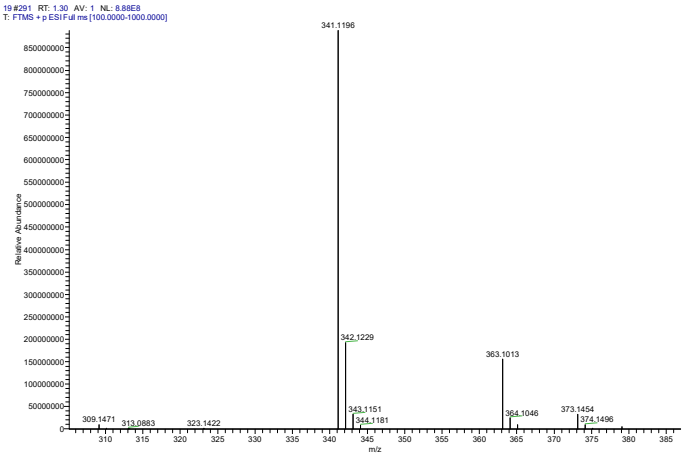
Prepared according to general procedure from [(CuOTf)]$_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (39.2 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1-1:5) and obtained as a yellow solid (52.5 mg, 77%), mp: 84.5-86.5 °C.

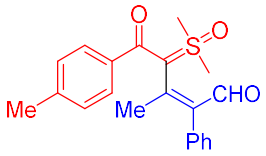
R$_f$ (ethyl acetate) = 0.3.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.60 – 7.57 (m, 2H), 7.39 – 7.35 (m, 3H), 7.34 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 6.99 – 6.95 (m, 2H), 3.68 (s, 6H), 1.93 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.5, 184.7, 148.5, 144.8, 140.1, 135.9, 130.5, 129.4, 128.3, 128.2, 127.6, 127.5, 84.6, 43.5, 42.9, 26.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}O_3S$ 341.1206; Found 341.1196.





(Z)-4-(Dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxo-2-phenyl-5-(p-tolyl)pent-2-enal (3ia)

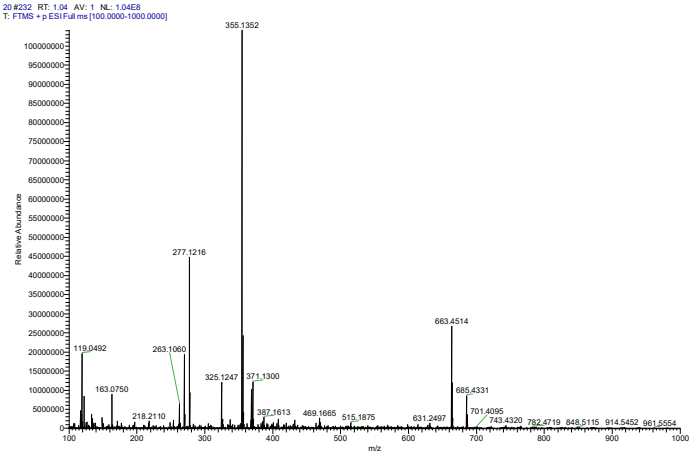
Prepared according to general procedure from [(CuOTf)]$_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(p-tolyl)ethan-1-one (42.0 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:1) and obtained as a yellow oil (44.4 mg, 63%).

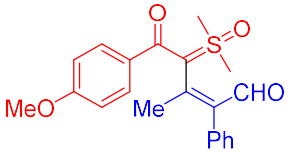
R_f (petroleum ether/ethyl acetate = 1:1) = 0.3.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.3 – 7.28 (m, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.03 – 7.00 (m, 2H), 3.67 (s, 6H), 2.36 (s, 3H), 1.91 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.5, 184.6, 148.7, 144.5, 140.9, 137.3, 136.0, 129.4, 129.0, 128.2, 127.7, 127.5, 84.4, 43.6, 43.0, 26.3, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}O_3S$ 355.1362; Found 355.1352.





(Z)-4-(Dimethyl(oxo)-λ^6-sulfaneylidene)-5-(4-methoxyphenyl)-3-methyl-5-oxo-2-phenylpent-2-enal (3ja)

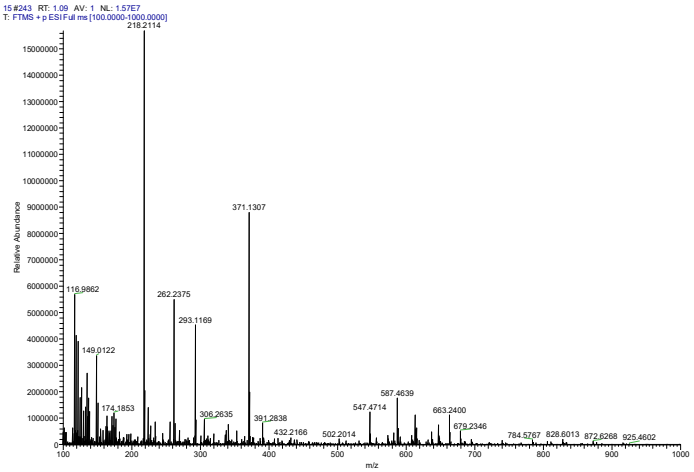
Prepared according to general procedure from [(CuOTf)]$_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(4-methoxyphenyl)ethan-1-one (45.2 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1-1:5) and obtained as a yellow solid (35.1 mg, 47%), mp: 187.2-189.2 °C.

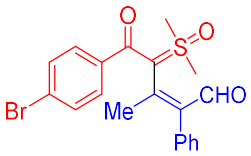
R_f (ethyl acetate) = 0.6.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.60 (d, *J* = 9.2 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 3.67 (s, 6H), 1.92 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.5, 183.9, 161.5, 148.6, 144.5, 136.0, 132.4, 129.6, 129.5, 128.2, 127.5, 113.5, 84.0, 55.4, 43.8, 43.1, 26.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}O_4S$ 371.1312; Found 371.1307.





(Z)-5-(4-Bromophenyl)-4-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxo-2-phenylpent-2-enal (3ka)

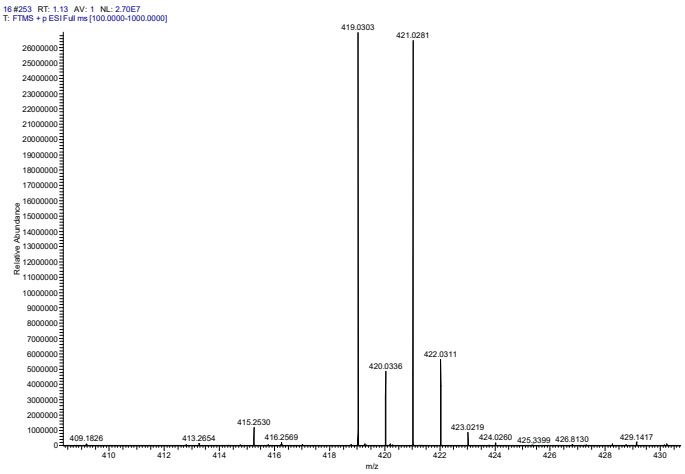
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), 1-(4-bromophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan-1-one (54.8 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1-1:5) and obtained as a yellow solid (33.7 mg, 40%), mp: 157.7-159.7 °C.

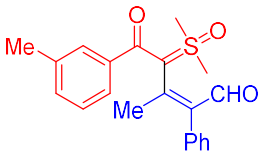
R_f (ethyl acetate) = 0.6.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 7.53 – 7.45 (m, 4H), 7.38 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 7.00 – 6.97 (m, 2H), 3.67 (s, 6H), 1.92 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.4, 183.0, 147.9, 144.9, 139.0, 135.6, 131.5, 129.3, 128.3, 127.7, 124.9, 84.9, 43.4, 42.7, 26.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}BrO_3S$ 419.0311; Found 419.0303.





(Z)-4-(Dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxo-2-phenyl-5-(m-tolyl)pent-2-enal (3la)

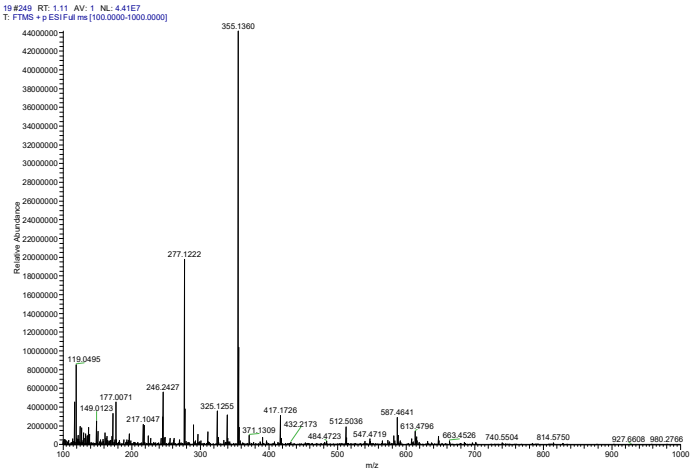
Prepared according to general procedure from [(CuOTf)]$_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(m-tolyl)ethan-1-one (42.0 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1-1:5) and obtained as a yellow solid (41.9 mg, 59%), mp: 97.1-99.1 °C.

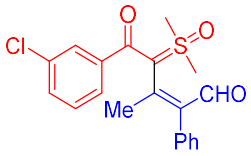
R$_f$ (ethyl acetate) = 0.5.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 7.41 – 7.32 (m, 4H), 7.30 – 7.25 (m, 2H), 7.21 – 7.19 (m, 1H), 6.99 – 6.95 (m, 2H), 3.67 (s, 6H), 2.35 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.5, 184.9, 148.8, 144.7, 140.0, 138.0, 135.9, 131.3, 129.3, 128.3, 128.2, 128.1, 127.5, 124.8, 84.5, 43.5, 42.9, 26.2, 21.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}O_3S$ 355.1362; Found 355.1360.





(Z)-5-(3-Chlorophenyl)-4-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxo-2-phenylpent-2-enal (3ma)

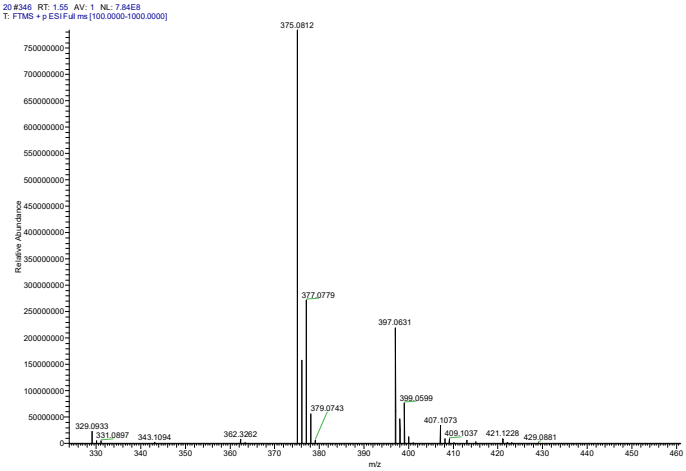
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), 1-(3-chlorophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan-1-one (46.0 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1-1:5) and obtained as a yellow solid (46.1 mg, 62%), mp: 113.2-115.2 °C.

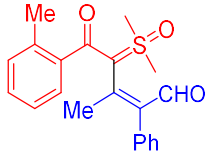
R_f (ethyl acetate) = 0.5.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.79 (s, 1H), 7.44 – 7.40 (m, 4H), 7.34 – 7.30 (m, 2H), 7.28 – 7.23 (m, 1H), 6.86 – 6.83 (m, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 1.94 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.4 182.6, 148.0, 145.1, 141.8, 135.7, 134.2, 130.4, 129.7, 129.3, 128.3, 127.8, 127.7, 125.8, 85.0, 43.2, 42.7, 26.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}ClO_3S$ 375.0816; Found 375.0812.





(Z)-4-(Dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxo-2-phenyl-5-(o-tolyl)pent-2-enal (3na)

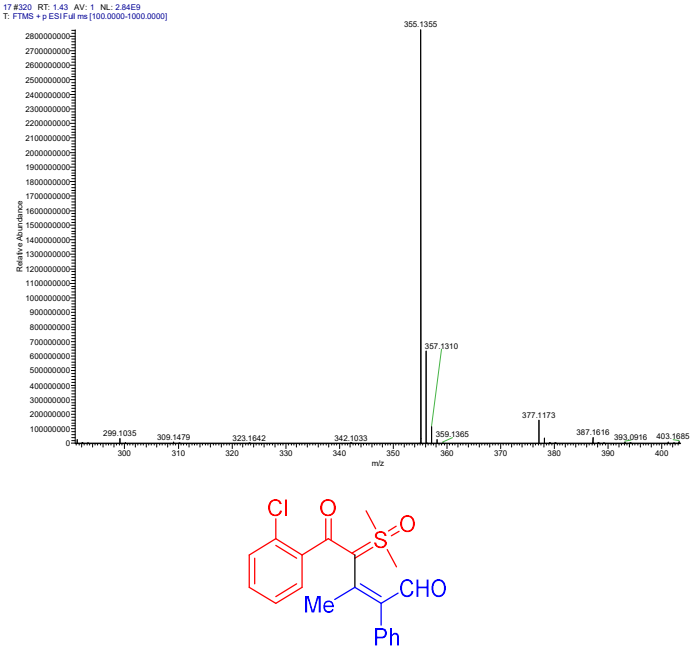
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(o-tolyl)ethan-1-one (42.0 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1-1:5) and obtained as a yellow solid (52.6 mg, 74%), mp: 177.9-179.9 °C.

R_f (ethyl acetate) = 0.4.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.87 (s, 1H), 7.28 – 7.17 (m, 4H), 7.15 – 7.11 (m, 3H), 6.68 – 6.64 (m, 2H), 3.85 (s, 3H), 3.52 (s, 3H), 2.27 (s, 3H), 1.86 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.3, 186.7, 148.6, 145.0, 140.1, 135.8, 135.6, 131.1, 129.3, 129.1, 128.1, 127.4, 126.9, 125.2, 86.2, 43.13, 43.07, 25.7, 19.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}O_3S$ 355.1362; Found 355.1355.



(Z)-5-(2-Chlorophenyl)-4-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-oxo-2-phenylpent-2-enal (3oa)

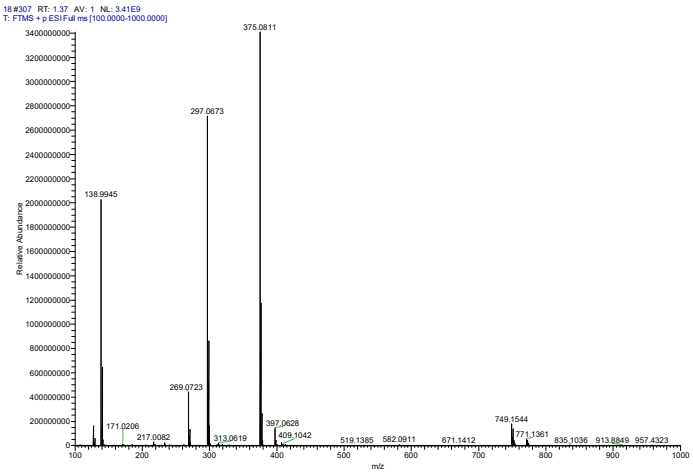
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), 1-(2-chlorophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan-1-one (46.0 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1-1:5) and obtained as a yellow solid (41.6 mg, 56%), mp: 154.2-156.2 °C.

R_f (ethyl acetate) = 0.6.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.04 (s, 1H), 7.37 – 7.35 (m, 1H), 7.30 – 7.23 (m, 6H), 6.75 (d, *J* = 7.2 Hz, 2H), 3.73 (s, 3H), 3.71 (s, 3H), 1.94 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.8, 182.5, 148.5, 145.5, 139.8, 135.7, 130.8, 130.1, 130.0, 129.3, 128.8, 128.2, 127.5, 126.8, 86.5, 43.3, 42.7, 25.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}ClO_3S$ 375.0816; Found 375.0811.



(Z)-4-(Dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-5-(naphthalen-2-yl)-5-oxo-2-phenylpent-2-enal (3pa)

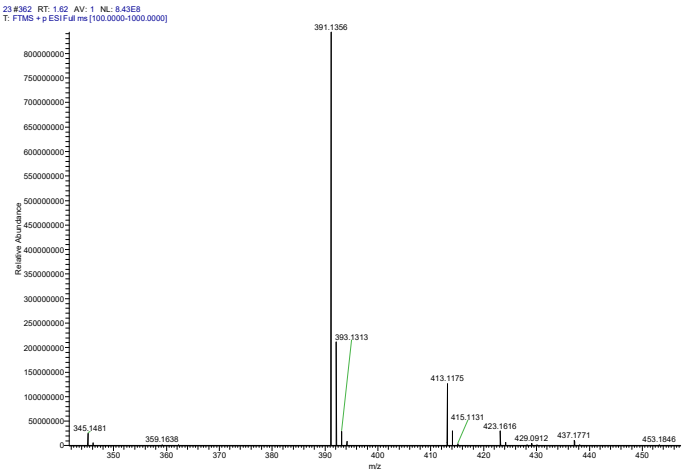
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(naphthalen-2-yl)ethan-1-one (49.2 mg, 0.2 mmol, 1.0 equiv), 4-ethynyl-4-phenyl-1,3-dioxolan-2-one (112.8 mg, 0.6 mmol, 3.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at 0 °C for 16 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1-1:5) and obtained as a yellow solid (49.1 mg, 63%), mp: 113.7-115.7 °C.

R_f (ethyl acetate) = 0.5.

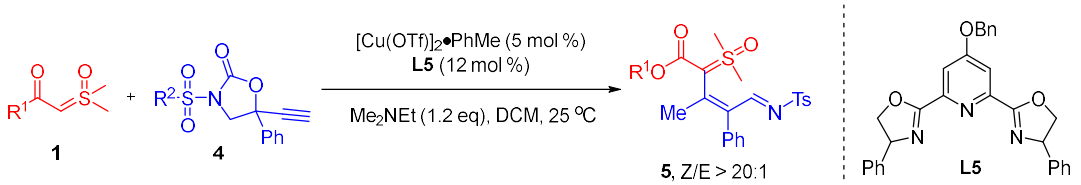
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.08 (s, 1H), 8.13 (d, *J* = 1.6 Hz, 1H), 7.87 – 7.82 (m, 3H), 7.70 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.25 (m, 1H), 7.00 – 6.96 (m, 2H), 3.71 (s, 6H), 1.93 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.5, 184.3, 148.4, 144.9, 137.4, 135.8, 134.3, 132.7, 129.4, 128.8, 128.2, 128.14, 128.05, 127.8, 127.5, 127.3, 126.6, 124.6, 84.9, 43.6, 42.9, 26.4.

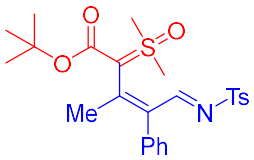
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}O_3S$ 391.1362; Found 391.1356.



General Procedure for the Synthesis of Compounds 5



To a dry Schlenk tube were added $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%) and dry DCM (1.0 mL). The resulting mixture was stirred at room temperature for 0.5 h. Then **1** (0.2 mmol, 1.0 equiv), **4** (0.4 mmol, 2.0 equiv), Me_2NEt (17.5 mg, 0.24 mmol, 1.2 equiv) and dry DCM (3.0 mL) were added sequentially to the above solution at room temperature. The resulting mixture was stirred at RT for 2 h. After this time, The reaction mixture was concentrated under vacuum; the crude residue was purified by silica gel column chromatography to give **5**.



tert-Butyl (Z)-2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-3-methyl-4-((4-methylphenyl)sulfonamido)-4-phenylbut-3-enoate (5aa)

Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), tert-butyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 5-ethynyl-5-phenyl-3-tosyloxazolidin-2-one (136.4 mg, 0.4 mmol, 2.0 equiv), Me_2NEt (17.5 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at RT for 2 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1-1:1) and obtained as a yellow solid (75.2 mg, 77%), mp: 188.8-190.8 °C.

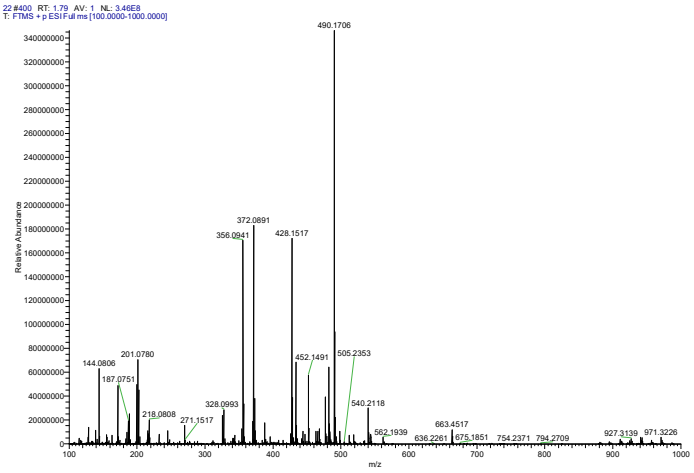
R_f (petroleum ether/ethyl acetate = 1:1) = 0.5.

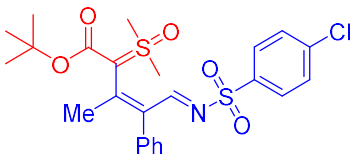
^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.03 (s, 1H), 7.73 – 7.70 (m, 2H), 7.30 – 7.22 (m, 5H), 7.10 – 7.06 (m, 2H), 3.58 (s, 3H), 3.48 (s, 3H), 2.38 (s, 3H), 2.09 (s, 3H), 1.47 (s, 9H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 170.1, 165.1, 153.4, 143.4, 137.7, 137.0, 136.8, 130.3,

129.4, 128.0, 127.4, 127.2, 80.2, 71.0, 44.3 28.8, 24.6, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{32}NO_5S_2$ 490.1716; Found 490.1706.





tert-Butyl (Z)-4-((4-chlorophenyl)sulfonamido)-2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-3-methyl-4-phenylbut-3-enoate (5ab)

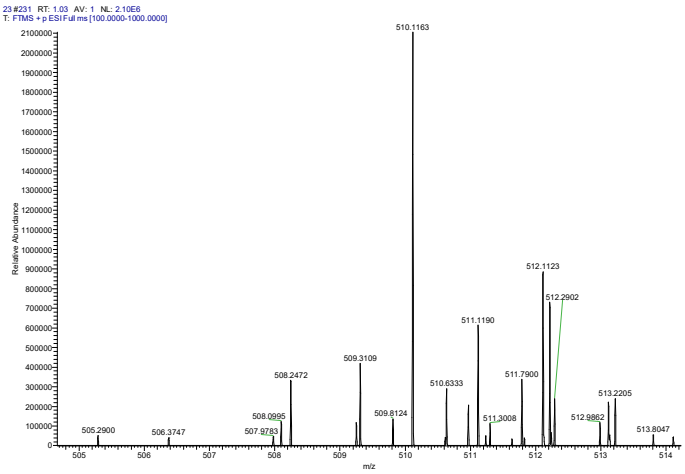
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), tert-butyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 3-((4-chlorophenyl)sulfonyl)-5-ethynyl-5-phenyloxazolidin-2-one (144.4 mg, 0.4 mmol, 2.0 equiv), Me_2NEt (17.6 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at RT for 2 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1-1:1) and obtained as a yellow solid (86.2 mg, 85%), mp: 173.6-175.6 °C.

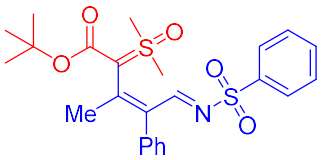
R_f (petroleum ether/ethyl acetate = 1:1) = 0.6.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.02 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.33 – 7.25 (m, 3H), 7.08 (d, *J* = 6.8 Hz, 2H), 3.60 (s, 3H), 3.45 (s, 3H), 2.10 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.5, 165.1, 154.5, 141.2, 139.0, 138.5, 137.3, 130.2, 129.0, 128.8, 128.1, 127.3, 80.4, 71.7, 44.4, 28.7, 24.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}ClNO_5S_2$ 510.1170; Found 510.1163.





tert-Butyl (Z)-2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-3-methyl-4-phenyl-4-(phenylsulfonamido) but-3-enoate (5ac)

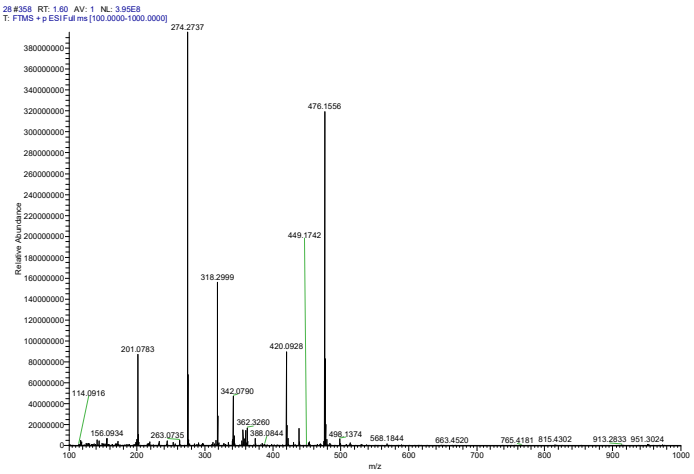
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), tert-butyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 5-ethynyl-5-phenyl-3-(phenylsulfonyl)oxazolidin-2-one (65.4 mg, 0.4 mmol, 2.0 equiv), Me_2NEt (17.6 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at RT for 2 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1-1:1) and obtained as a yellow solid (64.8 mg, 68%), mp: 196.1-198.1 °C.

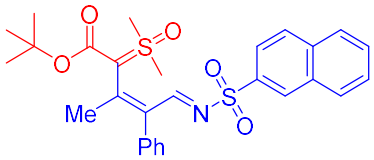
R_f (petroleum ether/ethyl acetate = 1:1) = 0.5.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.84 (s, 1H), 7.79 – 7.76 (m, 2H), 7.69 – 7.64 (m, 1H), 7.59 – 7.55 (m, 2H), 7.37 – 7.33 (m, 2H), 7.310 – 7.26 (m, 1H), 7.05 – 7.03 (m, 2H), 3.63 (s, 6H), 2.01 (s, 3H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 170.5, 164.2, 157.1, 139.5, 137.5, 136.5, 133.6, 130.3, 129.7, 128.6, 127.7, 127.5, 79.6, 75.7, 43.8, 28.8, 24.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}NO_5S_2$ 476.1560; Found 476.1556.





tert-Butyl (Z)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-4-(naphthalene-2-sulfonamido)-4-phenylbut-3-enoate (5ad)

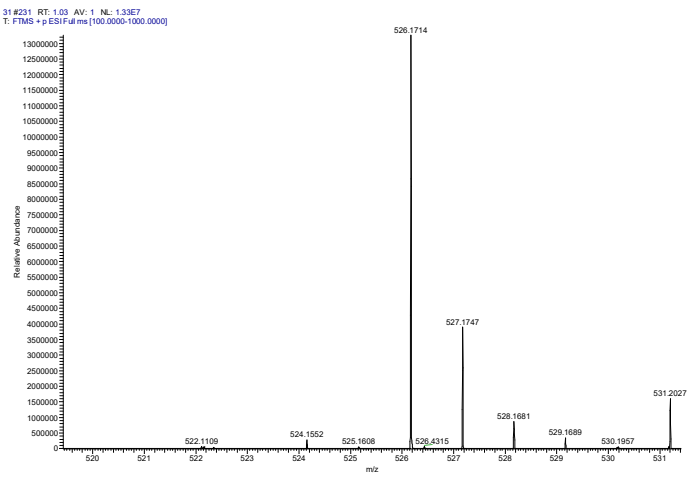
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), tert-butyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 5-ethynyl-3-(naphthalen-2-ylsulfonyl)-5-phenyloxazolidin-2-one (150.8 mg, 0.4 mmol, 2.0 equiv), Me_2NEt (17.6 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at RT for 2 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2:1-1:2) and obtained as a yellow oil (78.4 mg, 75%).

R_f (petroleum ether/ethyl acetate = 1:1) = 0.4.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.89 (s, 1H), 8.52 – 8.46 (m, 1H), 8.16 – 8.04 (m, 3H), 7.77 – 7.67 (m, 3H), 7.36 – 7.32 (m, 2H), 7.30 – 7.25 (m, 1H), 7.07 – 7.04 (m, 2H), 3.62 (s, 6H), 2.02 (s, 3H), 1.40 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 170.5, 164.2, 157.1, 137.5, 136.6, 136.5, 134.9, 132.1, 130.3, 129.79, 129.76, 129.6, 128.7, 128.6, 128.3, 128.1, 127.6, 123.0, 79.6, 75.8, 45.2, 28.8, 24.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{32}NO_5S_2$ 526.1716; Found 526.1714.



tert-Butyl (Z)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-(ethylsulfonamido)-3-methyl-4-phenylbut-3-enoate (5ae)

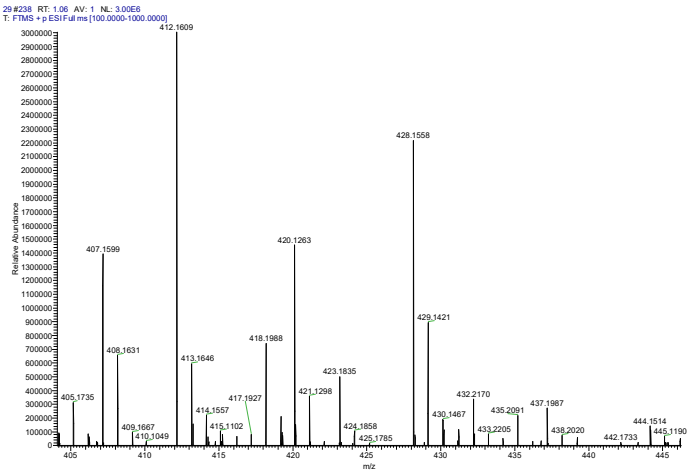
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), tert-butyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 3-(ethylsulfonyl)-5-ethynyl-5-phenyloxazolidin-2-one (111.6 mg, 0.4 mmol, 2.0 equiv), Me_2NEt (17.6 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at RT for 2 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1-1:1) and obtained as a yellow oil (62.8 mg, 74%).

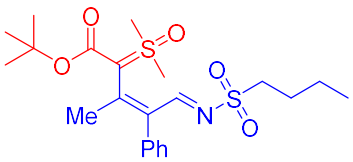
R_f (petroleum ether/ethyl acetate = 1:1) = 0.5.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.79 (s, 1H), 7.41 – 7.38 (m, 2H), 7.33 – 7.29 (m, 1H), 7.14 – 7.11 (m, 2H), 3.63 (s, 6H), 3.03 (q, J = 7.2 Hz, 2H), 2.02 (s, 3H), 1.42 (s, 9H), 1.11 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 171.8, 164.3, 155.6, 137.7, 136.8, 130.4, 128.6, 127.6, 79.5, 74.5, 49.2, 46.7, 28.8, 24.7, 8.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{30}NO_5S_2$ 428.1560; Found 428.1558.





tert-Butyl (Z)-4-(butylsulfonamido)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-4-phenylbut-3-enoate (5af)

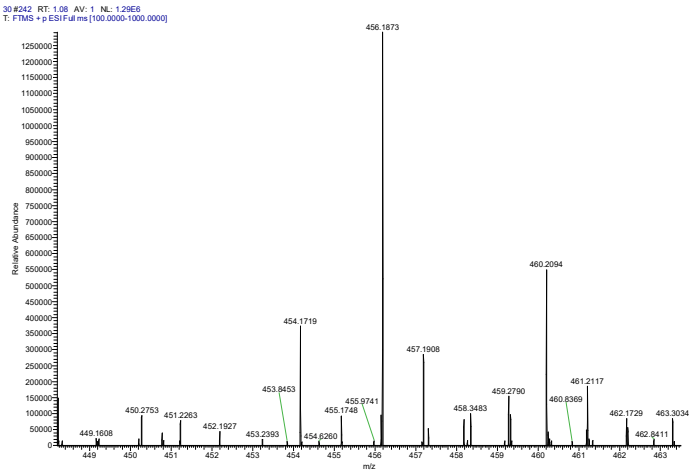
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), tert-butyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (38.4 mg, 0.2 mmol, 1.0 equiv), 3-(butylsulfonyl)-5-ethynyl-5-phenyloxazolidin-2-one (122.8 mg, 0.4 mmol, 2.0 equiv), Me_2NEt (17.6 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at RT for 2 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1-1:1) and obtained as a yellow oil (73.4 mg, 81%).

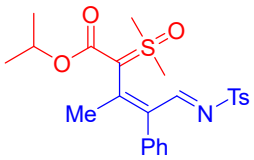
R_f (petroleum ether/ethyl acetate = 1:1) = 0.6.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.80 (s, 1H), 7.41 – 7.37 (m, 2H), 7.33 – 7.29 (m, 1H), 7.14 – 7.11 (m, 2H), 3.63 (s, 6H), 3.04 – 3.00 (m, 2H), 2.02 (s, 3H), 1.59 – 1.51 (m, 2H), 1.42 (s, 9H), 1.33 (q, J = 7.2 Hz, 2H), 0.84 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 171.6, 164.3, 155.5, 137.7, 136.9, 130.4, 128.6, 127.6, 79.4, 74.5, 51.9, 43.8, 28.8, 25.2, 24.7, 21.2, 13.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{34}NO_5S_2$ 456.1873; Found 456.1873.





Isopropyl (Z)-2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-3-methyl-4-((4-methylphenyl)sulfonamido)-4-phenylbut-3-enoate (5ba)

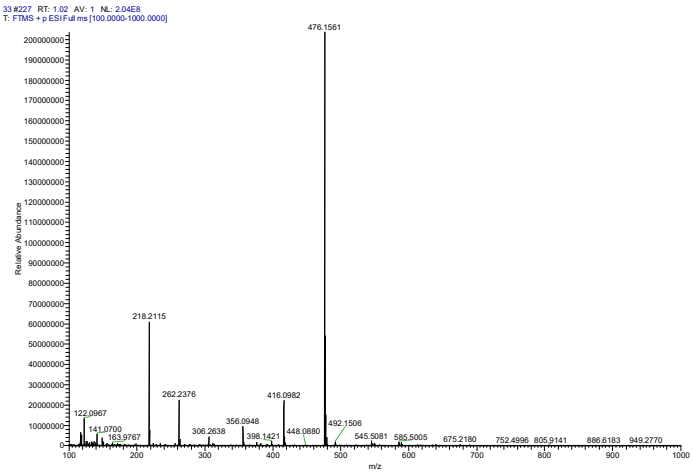
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), isopropyl 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)acetate (35.6 mg, 0.2 mmol, 1.0 equiv), 5-ethynyl-5-phenyl-3-tosyloxazolidin-2-one (136.4 mg, 0.4 mmol, 2.0 equiv), Me_2NEt (17.6 mg, 0.24 mmol, 1.2 equiv) in DCM (4.0 mL) at RT for 2 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2:1-1:2) and obtained as a yellow solid (66.6 mg, 70%), mp: 142.3-144.3 °C.

R_f (ethyl acetate) = 0.5.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.77 (s, 1H), 7.69 – 7.60 (m, 2H), 7.39 – 7.34 (m, 4H), 7.31 – 7.27 (m, 1H), 7.06 – 7.03 (m, 2H), 4.88 (p, J = 6.2 Hz, 1H), 3.62 (s, 6H), 2.37 (s, 3H), 2.01 (s, 3H), 1.17 (d, J = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 170.0, 164.0, 156.1, 144.1, 137.3, 137.1, 136.2, 130.3, 130.2, 128.6, 127.7, 74.1, 66.5, 43.2, 24.7, 22.4, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{30}NO_5S_2$ 476.1560; Found 476.1561.



Benzyl (Z)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)-3-methyl-4-((4-methylphenyl)sulfonamido)-4-phenylbut-3-enoate (5ca)

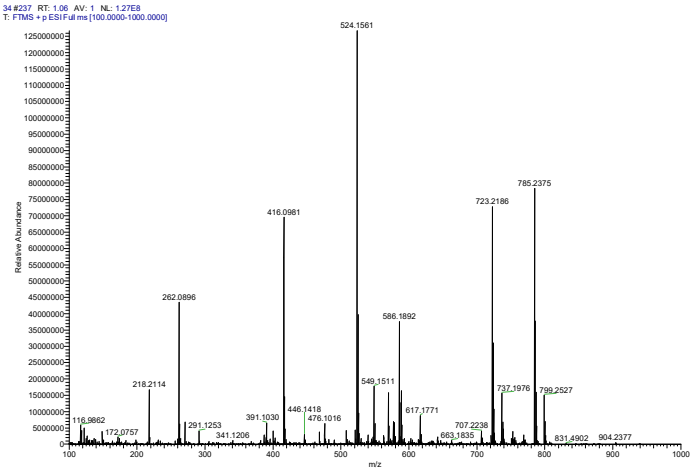
Prepared according to general procedure from $[(CuOTf)]_2$•PhMe (5.2 mg, 0.01 mmol, 5 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), benzyl 2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetate (45.2 mg, 0.2 mmol, 1.0 equiv), 5-ethynyl-5-phenyl-3-tosyloxazolidin-2-one (136.4 mg, 0.4 mmol, 2.0 equiv), Me_2NEt (17.6 mg, 0.24 mmol, 1.2 equiv) in DCM (2.0 mL) at RT for 2 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2:1-1:2) and obtained as a yellow oil (61.6 mg, 59%).

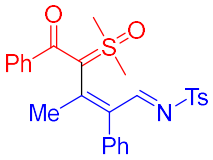
R_f (ethyl acetate) = 0.6.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.83 (s, 1H), 7.66 – 7.60 (m, 2H), 7.36 – 7.28 (m, 10H), 7.04 – 7.02 (m, 2H), 5.07 (s, 2H), 3.63 (s, 6H), 2.35 (s, 3H), 2.01 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 170.3, 164.0, 155.7, 144.2, 137.8, 137.4, 137.1, 135.9, 130.3, 130.2, 129.7, 128.8, 128.6, 128.2, 128.0, 127.8, 73.7, 64.9, 42.8, 24.9, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NO_5S_2$ 524.1560; Found 524.1561.





(Z)-N-(3-(Dimethyl(oxo)-λ^6-sulfaneylidene)-2-methyl-4-oxo-1,4-diphenylbut-1-en-1-yl)-4-methylbenzenesulfonamide (5da)

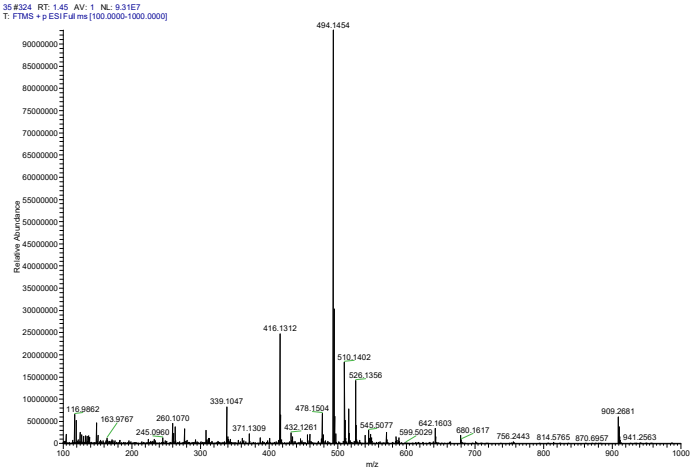
Prepared according to general procedure from $Cu(OTf)_2$ (7.2 mg, 0.02 mmol, 10 mol%), **L5** (11.4 mg, 0.024 mmol, 12 mol%), 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (39.2 mg, 0.2 mmol, 1.0 equiv), 5-ethynyl-5-phenyl-3-tosyloxazolidin-2-one (136.4 mg, 0.4 mmol, 2.0 equiv), Et_3N (24.3 mg, 0.24 mmol, 1.2 equiv) in cyclohexane/DCM (v/v = 4:1, 4.0 mL) at RT for 4 h. The desired product was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1:1-1:5) and obtained as a yellow oil (70.4 mg, 71%).

R_f (ethyl acetate) = 0.6

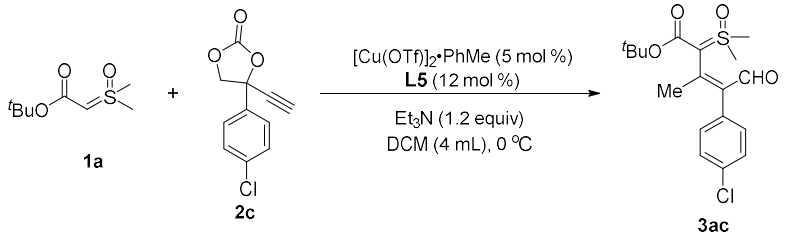
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.16 (s, 1H), 7.72 – 7.64 (m, 2H), 7.56 – 7.53 (m, 2H), 7.39 – 7.32 (m, 2H), 7.31 – 7.27 (m, 3H), 7.26 – 7.21 (m, 3H), 7.01 – 6.98 (m, 2H), 3.77 (s, 3H), 3.70 (s, 3H), 2.39 (s, 3H), 1.87 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 184.7, 169.7, 152.3, 143.7, 143.1, 140.3, 140.1, 136.1, 136.0, 130.6, 129.6, 129.5, 128.3, 128.1, 127.6, 127.5, 86.6, 43.9, 43.0, 26.6, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{28}NO_4S_2$ 494.1454; Found 494.1454.



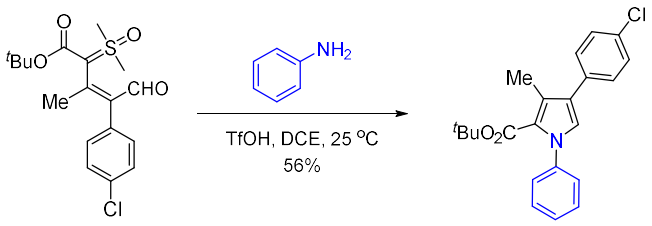
Gram-scale reaction



To a dry Schlenk tube were added $[(CuOTf)]_2$•PhMe (103 mg, 0.2 mmol, 5 mol%), **L5** (228 mg, 0.48 mmol, 12 mol%) and dry DCM (15 mL). The resulting mixture was stirred at room temperature for 0.5 h. Then **1a** (0.77 g, 4 mmol, 1.0 equiv), **2c** (2.67 g, 12 mmol, 3.0 equiv),

Et_3N (0.49 g, 4.8 mmol, 1.2 equiv) and dry DCM (50 mL) were added sequentially to the above solution at room temperature. The resulting mixture was stirred at 0 °C for 16 h. Then, the mixture was quenched with water and extracted with DCM. The combined organic layer was dried over anhydrous Na_2SO_4. The solid was filtered and the solvent was removed. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3:1-1:2) and **3ac** was obtained as a yellow solid (0.99 g, 67%).

Gram-scale and Further transformations



6

tert-Butyl 4-(4-chlorophenyl)-3-methyl-1-phenyl-1H-pyrrole-2-carboxylate (6)

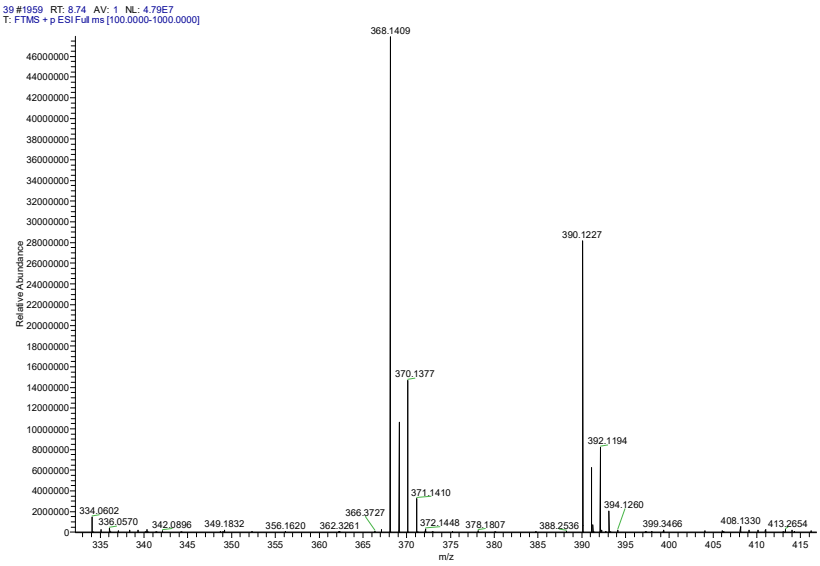
To a dry Schlenk tube were added **3ac** (37.0 mg, 0.1 mmol, 1.0 equiv.), aniline (11.0 mg, 0.12 mmol, 1.2 equiv.), TfOH (4.5 mg, 0.03 mmol, 0.3 equiv) and DCE (1 mL). The reaction was stirred at RT for 20 minutes. The reaction mixture was concentrated under vacuum; the crude residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 30:1-10:1) to give **6** as colorless oil (20.6 mg, 56%).

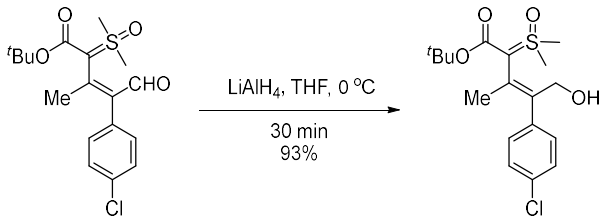
R_f (petroleum ether/ethyl acetate = 10:1) = 0.5.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.40 (m, 2H), 7.38 – 7.28 (m, 7H), 6.88 (s, 1H), 2.44 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.5, 141.6, 133.4, 132.2, 129.7, 128.7, 128.6, 127.4, 127.3, 126.0, 125.8, 125.1, 123.1, 80.7, 28.0, 11.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{23}ClNO_2$ 368.1412; Found 368.1409.





7

tert-Butyl (Z)-4-(4-chlorophenyl)-2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-5-hydroxy-3-methylpent-3-enoate (7)

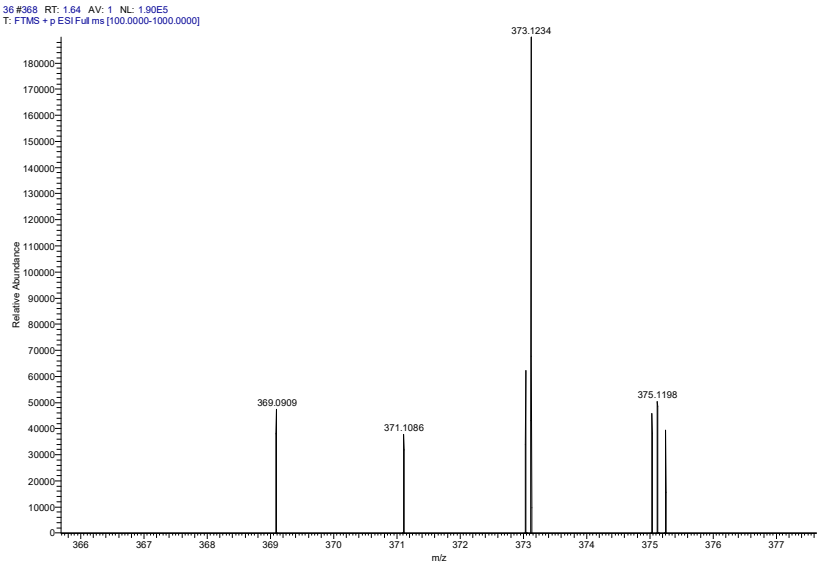
To a dry Schlenk tube were added $LiAlH_4$ (22.8 mg, 0.6 mmol, 3.0 equiv) and THF (1 mL) under Ar. Next, a solution of **3ac** (74.0 mg, 0.2 mmol, 1.0 equiv) in 3 mL of THF was slowly added dropwise to the reaction medium at 0 °C. The reaction was stirred for 30 min. After this time, quenched with NH_4Cl and filtered out the solid, the filtrate was extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, concentrated and purified by flash chromatography on silica gel to give **7** as colorless oil (69.2 mg, 93%).

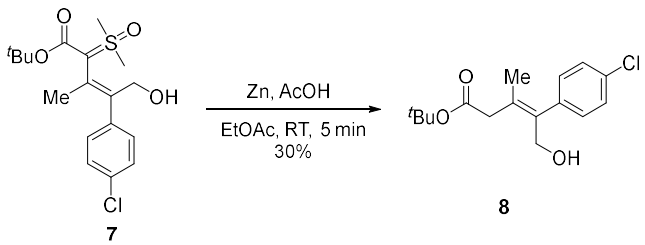
R_f (ethyl acetate) = 0.5.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 2H), 7.25 – 7.12 (m, 2H), 4.28 (s, 2H), 3.46 (s, 6H), 2.66 (s, 1H), 1.78 (s, 3H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 143.7, 140.1, 132.6, 123.0, 128.4, 79.0, 65.9, 42.8, 28.9, 23.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{26}ClO_4S$ 373.1235; Found 373.1234.





7 **8**

tert-Butyl (Z)-4-(4-chlorophenyl)-5-hydroxy-3-methylpent-3-enoate (8)

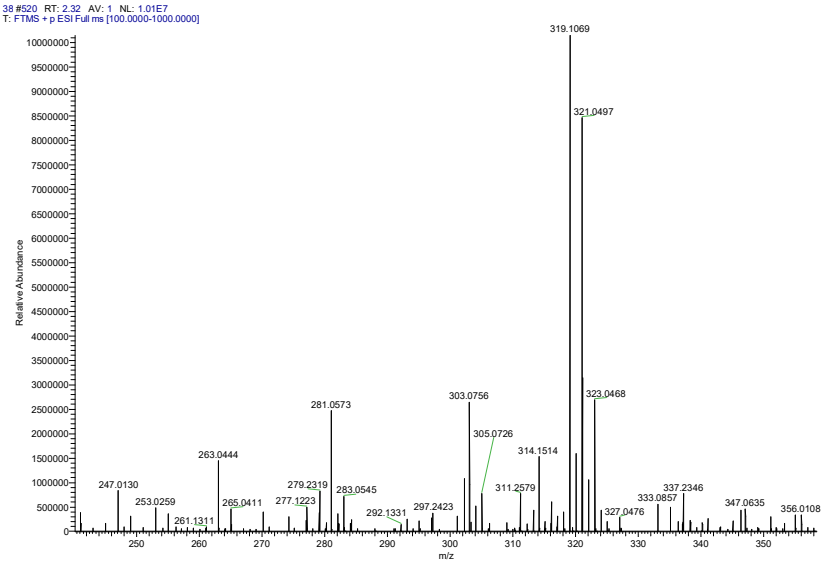
To a dry Schlenk tube, AcOH (260 mg, 2.0 mmol, 20.0 equiv) was added to a stirred mixture of **7** (74.4 mg, 0.2 mmol, 1.0 equiv) and Zn dust (240 mg, 2.0 mmol, 20.0 equiv) in EtOAc (2.0 mL) at room temperature. The reaction mixture was stirred overnight and filtered. The filtrate was washed with saturated $NaHCO_3$ solution and evaporate under vacuum. The crude product was purified by flash chromatography over silica gel using (petroleum ether / ethyl acetate = 10:1-3:1) to give **8** as colorless oil (17.8 mg, 30%).

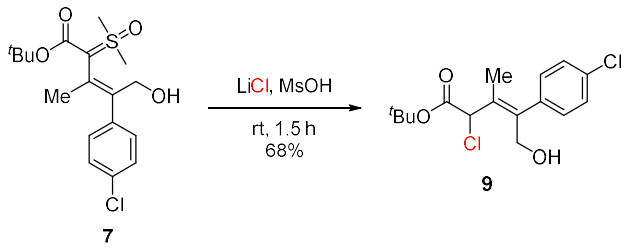
R_f (petroleum ether/ethyl acetate = 3:1) = 0.5.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.30 (m, 2H), 7.21 – 7.18 (m, 2H), 4.30 (d, *J* = 5.2 Hz, 2H), 3.23 (s, 2H), 2.84 (s, 1H), 1.69 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.8, 140.1, 138.6, 132.6, 130.6, 130.0, 128.4, 82.0, 63.9, 41.2, 28.0, 21.2.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{21}ClNaO_3$ 319.1071; Found 319.1069.





7 **9**

tert-Butyl (Z)-2-chloro-4-(4-chlorophenyl)-5-hydroxy-3-methylpent-3-enoate (9)

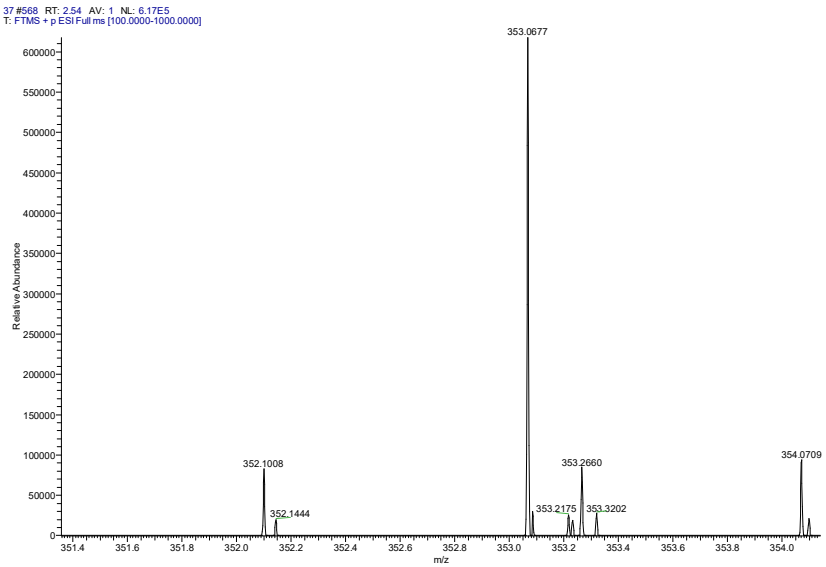
To stirred solution of ylide **7** (74.4 mg, 0.2 mmol, 1.0 equiv.) in dry THF (2 mL) at 0 °C was added LiCl (9.3 mg, 0.22 mmol, 1.1equiv.) and methanesulfonic acid (21.1 mg, 0.22 mmol, 1.1 equiv.). The reaction was stirred continued for 3 hours. After completion of the reaction, the mixture was evaporated under reduced pressure and dissolved in water. The crude mixture was extracted with EtOAc, dried over anhydrous Na_2SO_4 and solvent removed under reduced pressure. The crude product was purified by column chromatography (petroleum ether / ethyl acetate = 10:1-3:1) to afford **9** as colorless oil (44.9 mg, 68%).

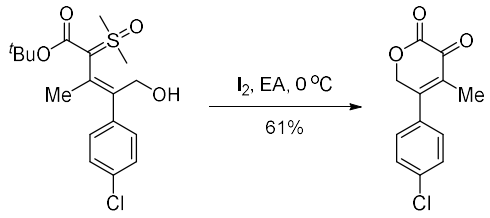
R_f (petroleum ether/ethyl acetate = 3:1) = 0.3.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 4H), 6.12 (s, 1H), 4.05 (d, *J* = 11.2 Hz, 1H), 3.93 (d, *J* = 11.2 Hz, 1H), 3.12 (s, 1H), 1.94 (s, 3H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 156.0, 139.7, 133.8, 128.7, 127.6, 118.3, 80.6, 79.4, 66.8, 28.2, 15.1.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{20}Cl_2NaO_3$ 353.0682; Found 353.0677.





7 10

5-(4-Chlorophenyl)-4-methyl-2H-pyran-2,3(6H)-dione (10)

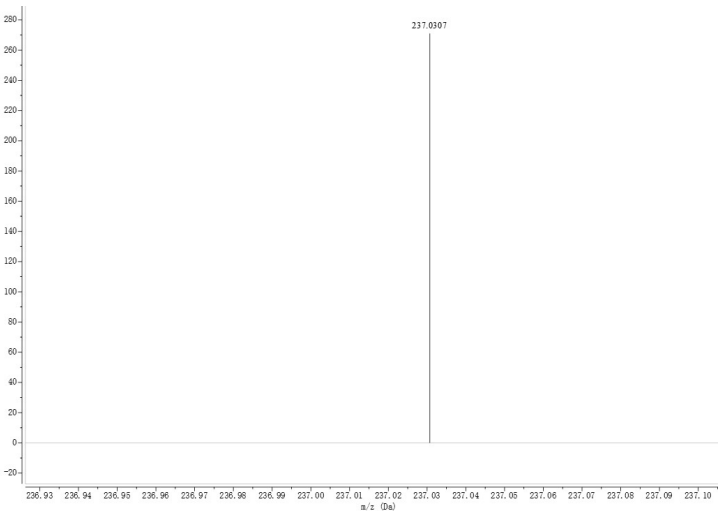
To a dry Schlenk tube were added **7** (74.4, 0.2 mmol, 1.0 equiv.), Iodine (50.8 mg, 0.2 mmol, 1.0 equiv.) and EtOAc (2 mL). The reaction was stirred at 0 °C for 10 minutes. Next, the reaction mixture was washed with a saturated solution of sodium thiosulfate. The organic phase was then concentrated under reduced pressure to furnish the crude product, that was purified by silica gel column chromatography to give **10** as colorless oil (29.0 mg, 61%).

R_f (petroleum ether/ethyl acetate = 1:1) = 0.6.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 7.29 – 7.25 (m, 2H), 4.28 – 4.13 (m, 2H), 2.04 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.1, 169.5, 135.4, 133.1, 129.4, 126.7, 93.8, 84.7, 64.1, 16.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}ClO_3$ 237.0313; Found 237.0307.



tert-Butyl (Z)-4-(4-chlorophenyl)-5-hydroxy-3-methyl-2-(p-tolylthio)pent-3-enoate (11)

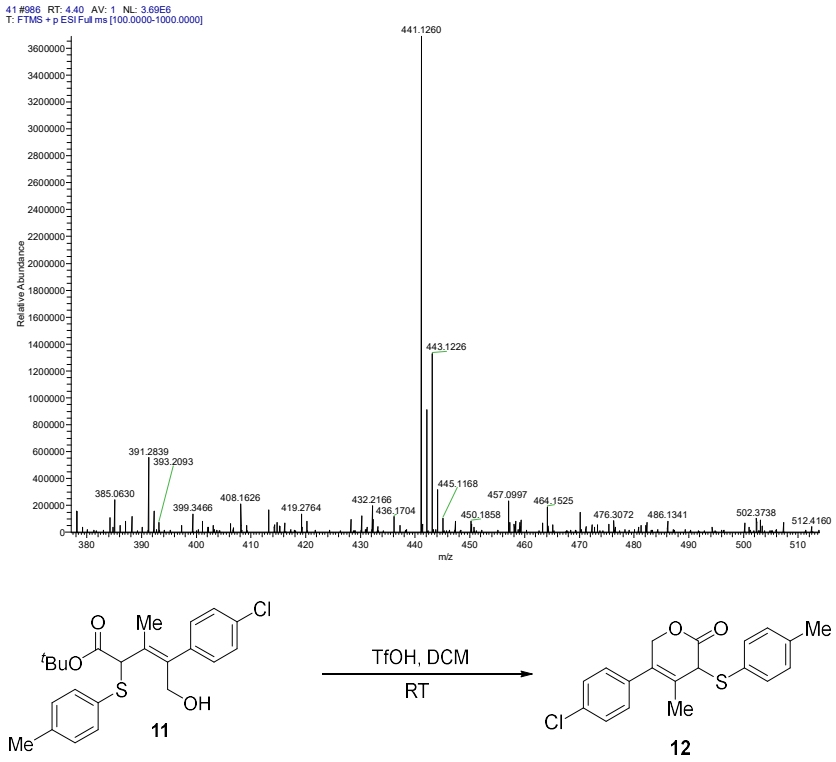
To a flask were added **7** (74.4 mg, 0.2 mmol, 1.0 equiv.), 4-Methylbenzenethiol (49.7 mg, 0.4 mmol, 2.0 equiv) and MeCN (4.0 mL). The reaction mixture was stirred at rt for 3h. The reaction mixture was concentrated under vacuum; the crude residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 15:1-5:1) to give **11** as white solid (52.3 mg, 63%), mp:126.5-128.5 °C.

R_f (petroleum ether/ethyl acetate = 3:1) = 0.3.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 5.02 (s, 1H), 4.03 (d, *J* = 12.8 Hz, 1H), 3.87 (d, *J* = 12.8 Hz, 1H), 2.35 (s, 3H), 1.72 (s, 3H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 139.9, 139.6, 139.0, 134.7, 132.9, 131.5, 129.9, 129.8, 129.5, 128.5, 83.3, 62.9, 56.9, 27.9, 21.2, 16.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{27}ClO_3S$ 441.1262; Found 441.1260.



5-(4-Chlorophenyl)-4-methyl-3-(p-tolylthio)-3,6-dihydro-2H-pyran-2-one (12)

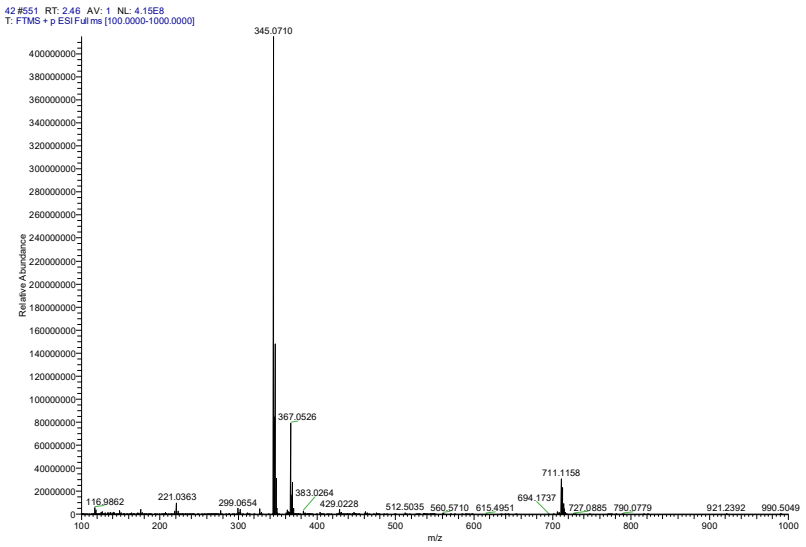
To a dry Schlenk tube were added **11** (41.8 mg, 0.1 mmol, 1.0 equiv.), TfOH (4.5 mg, 0.03 mmol, 0.3 equiv) and DCM (1 mL). The reaction was stirred at RT for 15 minutes. The reaction mixture was concentrated under vacuum; the crude residue was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 15:1-5:1) to give **12** as white solid (31.3 mg, 91%), mp:174.2-176.2 °C.

R_f (petroleum ether/ethyl acetate = 5:1) = 0.6.

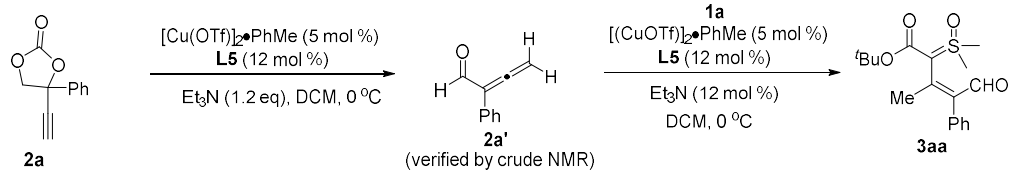
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.48 (m, 2H), 7.37 – 7.33 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.00 – 6.97 (m, 2H), 4.52 (dp, *J* = 16.0, 1.6 Hz, 1H), 4.25 (dp, *J* = 16.0, 1.6 Hz, 1H), 3.99 (s, 1H), 2.38 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 140.4, 136.1, 134.4, 134.1, 132.2, 130.0, 129.7, 128.9, 127.0, 126.8, 71.3, 50.4, 21.4, 17.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{18}ClO_2S$ 345.0711; Found 345.0710.



Scheme 6 Control experiments



Step 1: To a dry Schlenk tube were added $[(CuOTf)]_2$•PhMe (52.0 mg, 0. 1 mmol, 5 mol %), **L5** (114.0 mg, 0.12 mmol, 12 mol %) and dry DCM (1.0 mL). The resulting mixture was stirred at room temperature for 0.5 h. Then **2a** (3.0 mmol, 3.0 equiv), Et_3N (243.0 mg, 1.2 mmol, 1.2 equiv) and dry DCM (3.0 mL) were added sequentially to the above solution at room temperature. The resulting mixture was stirred at 0 °C for 2 h. The reaction mixture was concentrated under vacuum and the allenic aldehyde **2a′** (extremely unstable) was verified by crude NMR (32% yield).

Step 2: 1a (0.05 mmol, 1.0 equiv) and **2a′** (0.5 mmol, 10.0 equiv) were used as the substrates under different reaction conditions. The resulting mixture was stirred at 0 °C for 12 h. The reaction mixture was concentrated under vacuum; the crude residue was purified by silica gel column chromatography to give **3aa**. All the results were summarized in **Table S1**

Table S1. The controlled experiments of allenic aldehyde intermediate

entry	Variation from "standard reaction conditions"	yield (%)[b]
1	w/o Et_3N	54
2	w/o [Cu]/**L5**	49
3	w/o **L5**	57
4	w/o [Cu]/**L5** Et_3N	62

[a]Standard reaction conditions: **1a** (0.05 mmol,), **S5** (1.0 mmol), $[(CuOTf)]_2$•PhMe (5 mol %), **L5** (12 mol %), Et_3N

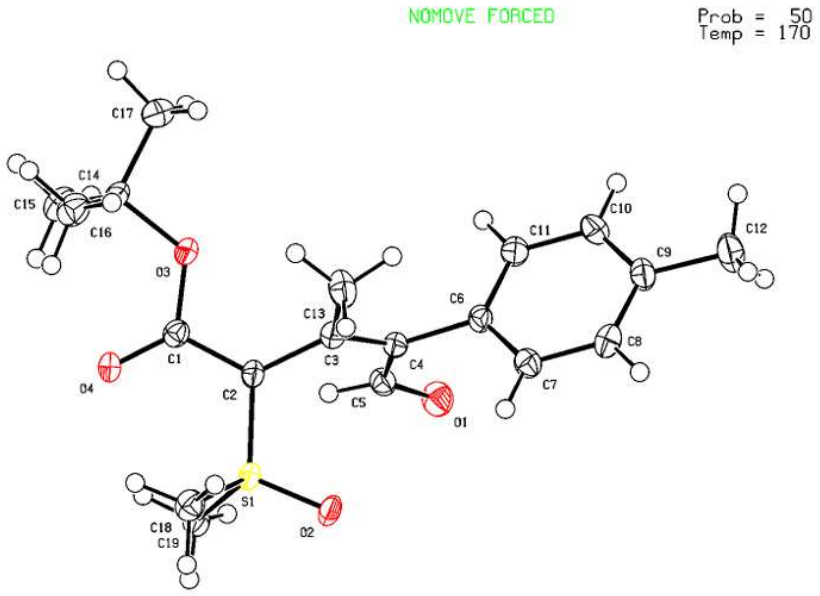
(0.12 mmol) in DCM (2 mL) at 0 °C under an argon atmosphere. [b]Isolated yields.

X-ray crystallographic data

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre: CCDC 2388075, (for **3ab**) and CCDC 2473172, (for **5ab**). The data can be obtained free of charge via the internet at https://www.ccdc.cam.ac.uk/structures/. The measurements were performed on a Bruker D8 Venture diffractometer. The structure solution and refinement were processed by SHELXL (2018/3).

X-ray crystallographic data of 3ab

Method of crystallization: A solution of **3ab** in ethyl acetate and petroleum ether was evaporated the solvent slowly at room temperature.



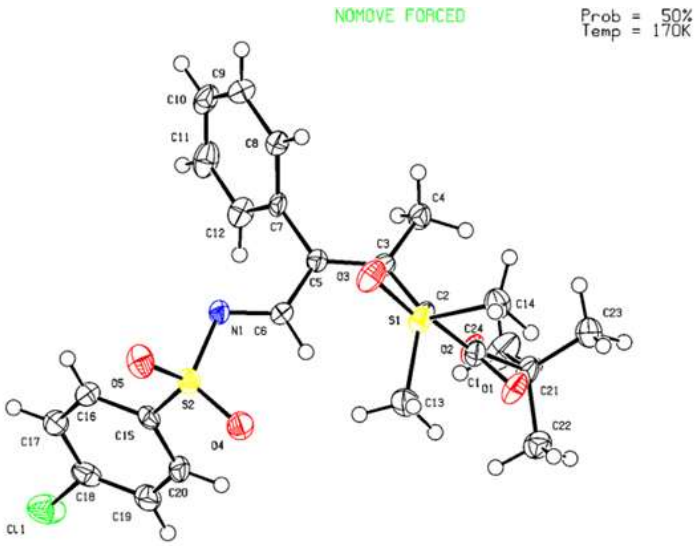
X-ray structure of **3ab**. Thermal ellipsoids are shown at the 50% level.

Empirical formula	C19H26O4S
Formula weight	350.46
Temperature/K	170.00
Crystal system	monoclinic
Space group	P21/c
a/Å	11.0456(2)
b/Å	5.83520(10)
c/Å	28.9629(5)
α/°	90
β/°	95.1620(10)
γ/°	90
Volume/Å3	1859.18(6)

Z	4
ρcalcg/cm3	1.252
μ/mm-1	1.112
F(000)	752.0
Crystal size/mm3	0.17 × 0.17 × 0.05
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	6.99 to 109.78
Index ranges	-12 ≤ h ≤ 13, -7 ≤ k ≤ 7, -35 ≤ l ≤ 33
Reflections collected	20574
Independent reflections	3522 [Rint = 0.0516, Rsigma = 0.0352]
Data/restraints/parameters	3522/0/224
Goodness-of-fit on F2	1.062
Final R indexes [I>=2σ (I)]	R1 = 0.0369, wR2 = 0.0880
Final R indexes [all data]	R1 = 0.0468, wR2 = 0.0931
Largest diff. peak/hole / e Å-3	0.30/-0.40

X-ray crystallographic data of 5ab

Method of crystallization: A solution of **5ab** in ethyl acetate and petroleum ether was evaporated the solvent slowly at room temperature.



X-ray structure of **5ab**. Thermal ellipsoids are shown at the 50% level.

Empirical formula	$C_{24}H_{28}ClNO_5S_2$
Formula weight	510.04
Temperature/K	170.00
Crystal system	monoclinic
Space group	P21/c
a/Å	12.4729(3)
b/Å	19.2544(4)
c/Å	11.3695(2)

α/°	90
β/°	114.8330(10)
γ/°	90
Volume/Å3	2478.01(9)
Z	4
ρcalcg/cm3	1.370
μ/mm-1	2.134
F(000)	1076.0
Crystal size/mm3	0.17 × 0.17 × 0.05
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	6.794 to 109.866
Index ranges	-15 ≤ h ≤ 14, -23 ≤ k ≤ 22, -13 ≤ l ≤ 13
Reflections collected	28262
Independent reflections	4699 [Rint = 0.1009, Rsigma = 0.0685]
Data/restraints/parameters	4699/0/304
Goodness-of-fit on F2	1.030
Final R indexes [I>=2σ (I)]	R1 = 0.0484, wR2 = 0.1161
Final R indexes [all data]	R1 = 0.0742, wR2 = 0.1289
Largest diff. peak/hole / e Å-3	0.44/-0.74

References

1. (a) Gong, Y.; Wang, C.; Zhou, F.; Liao, K.; Wang, X. Y.; Sun, Y.; Zhang, Y. X.; Tu, Z.; Wang, X.; Zhou, J. *Angew. Chem. Int. Ed.* **2023**, *62*, e202301470. (b) Tsuji, T.; Tanaka, T.; Tanaka, T.; Yazaki, R.; Ohshima, T. *Org. Lett.* **2020**, *22*, 4164-4170. (c) Willis, O. G.; Petri, F.; Rosa, D. F.; Mandoil, A.; Pal, R.; Zinna, F.; Bari, L. D. *J. Am. Chem. Soc.* **2023**, *145*, 25170-25176. (d) Surgenor, R. R.; Liu, X.; Keenlyside, M. J. H.; Myers, W.; Smith, M. D. *Nat. Chem.* **2023**, *15*, 357-365.
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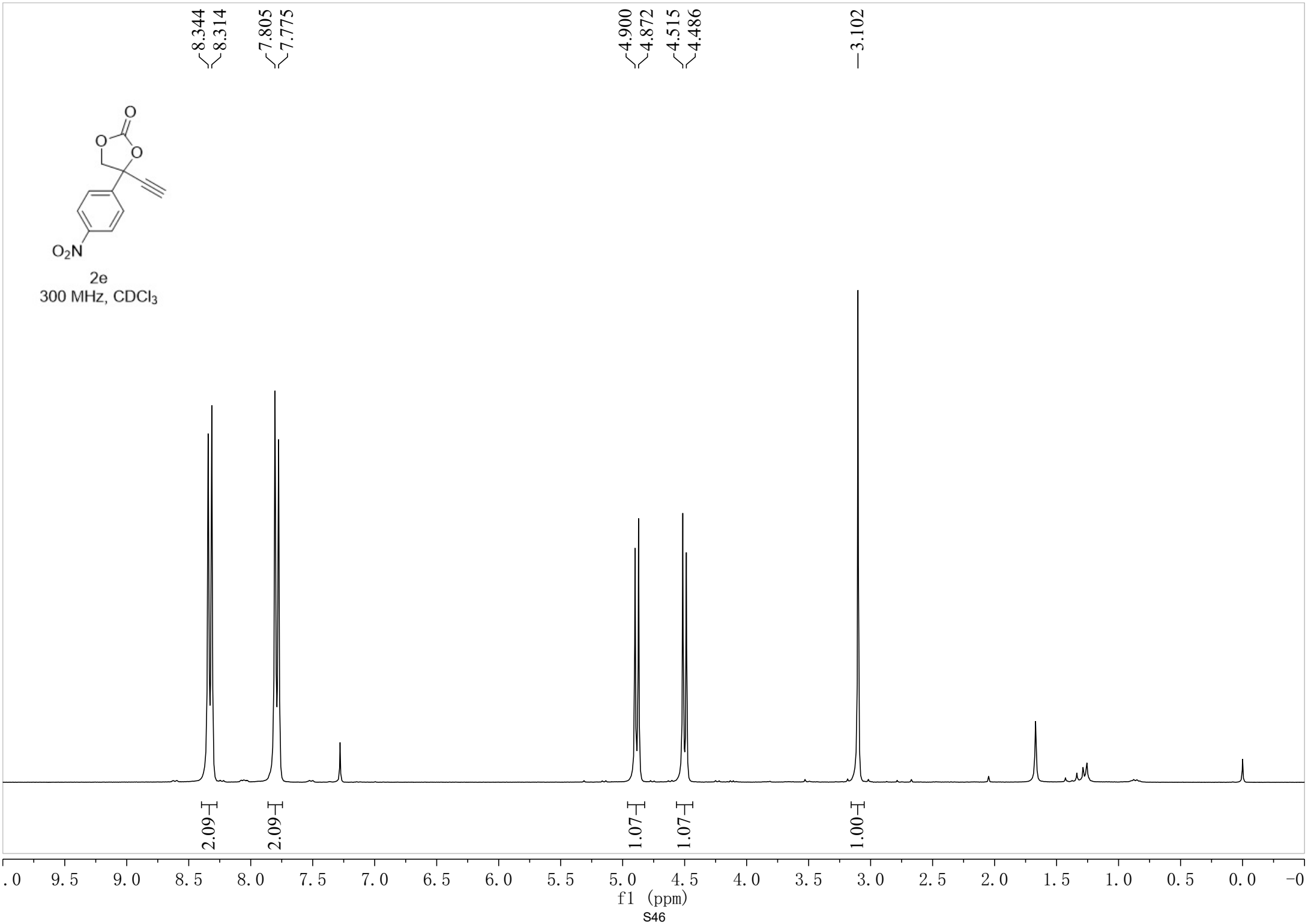
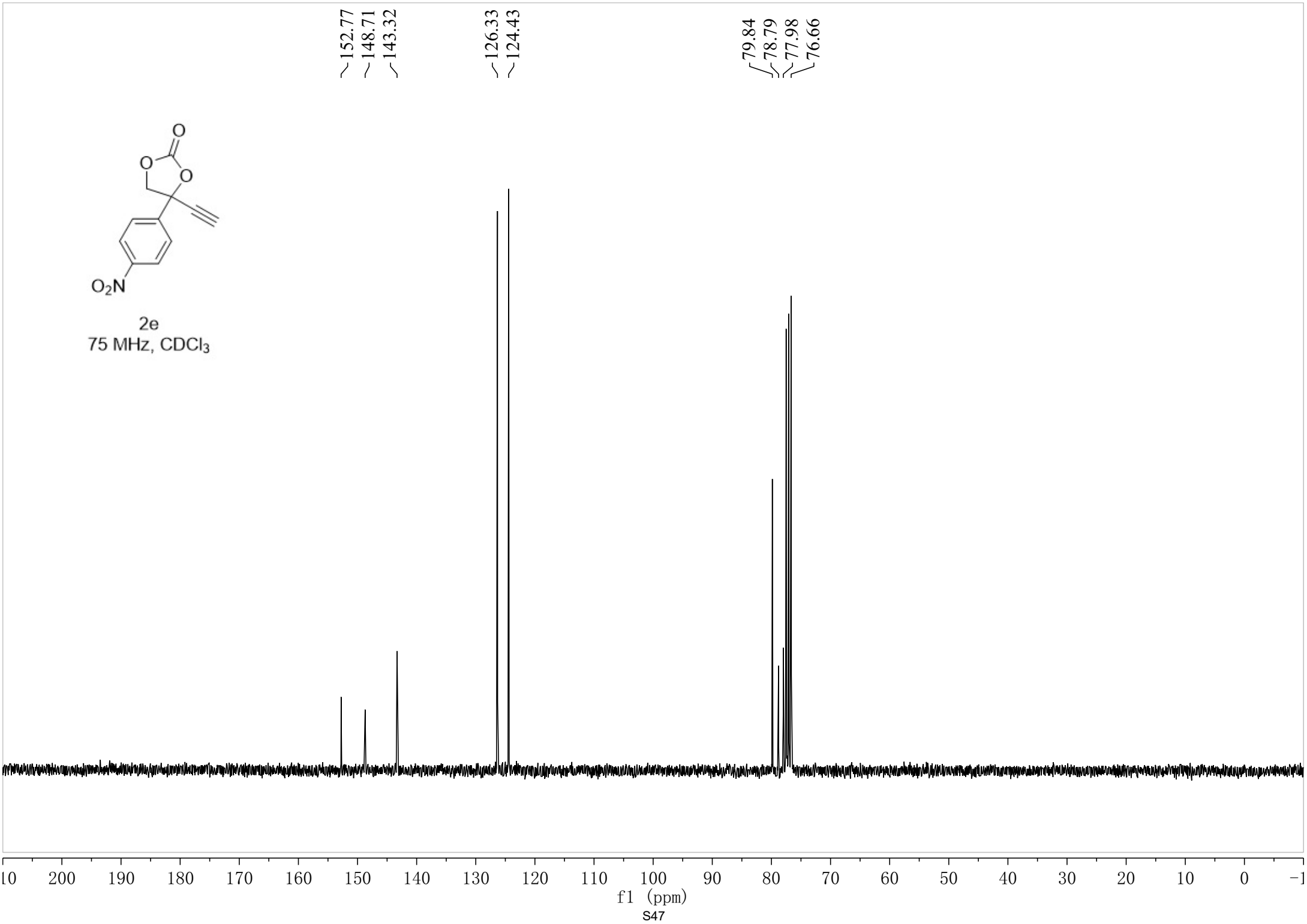
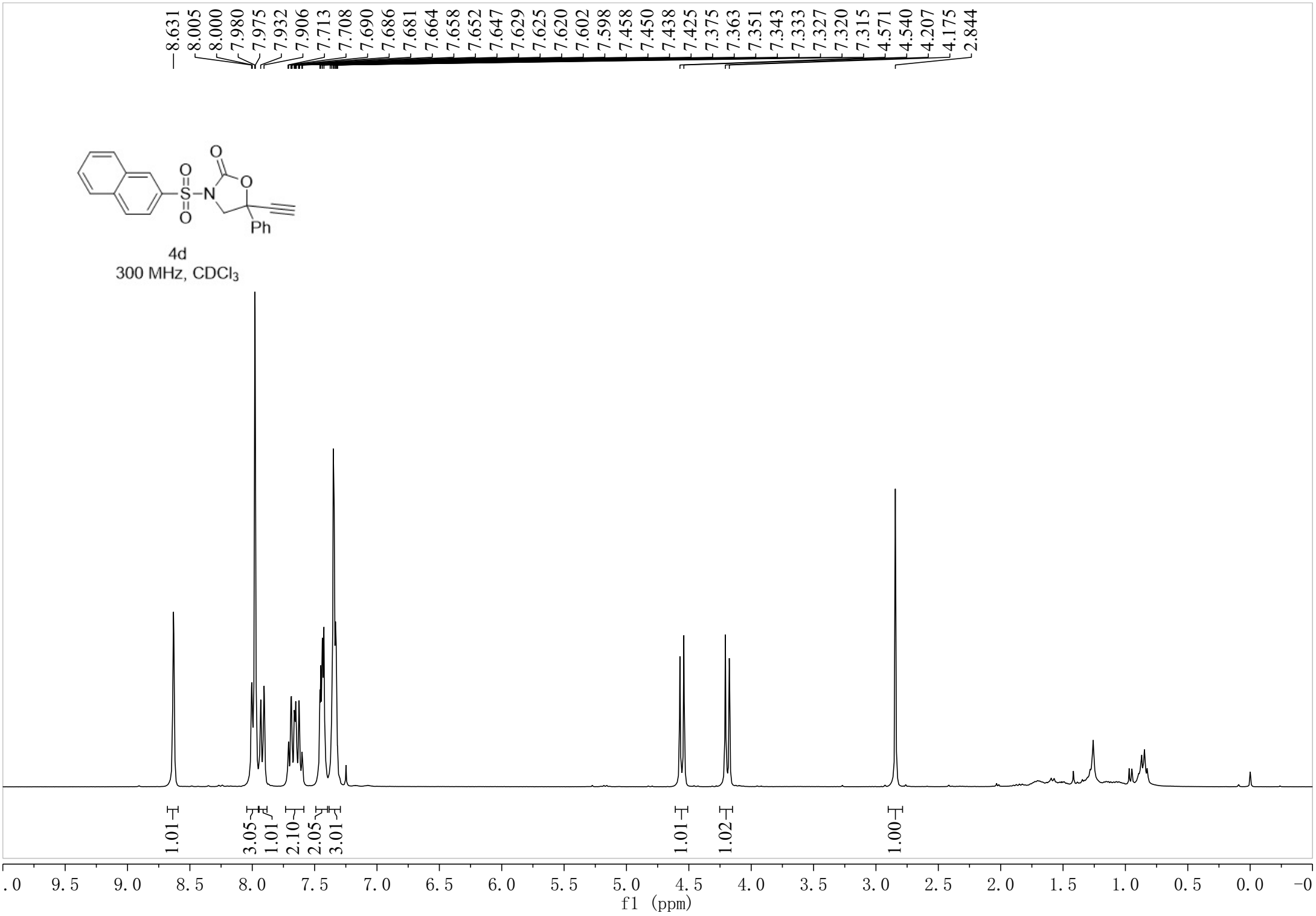
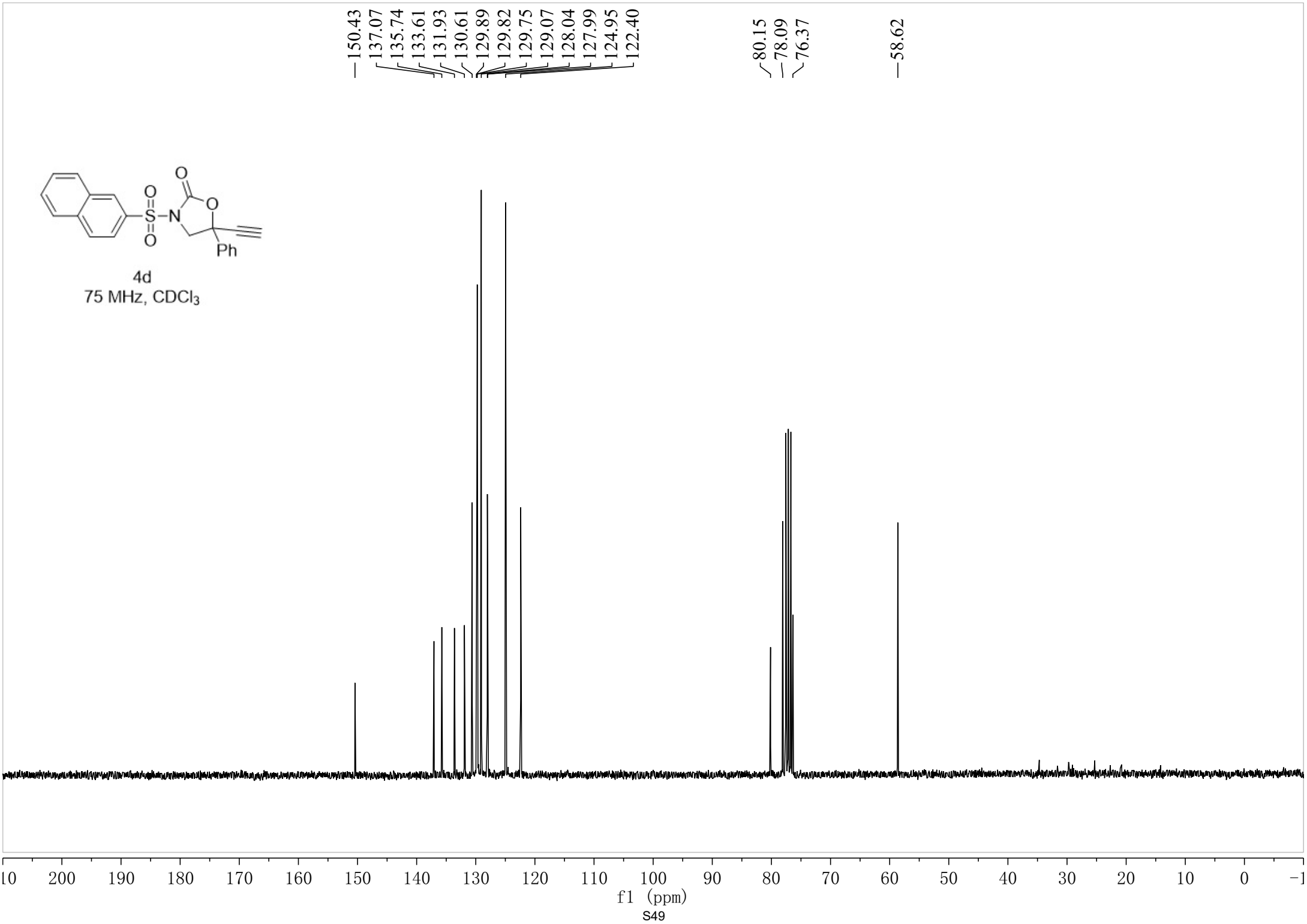
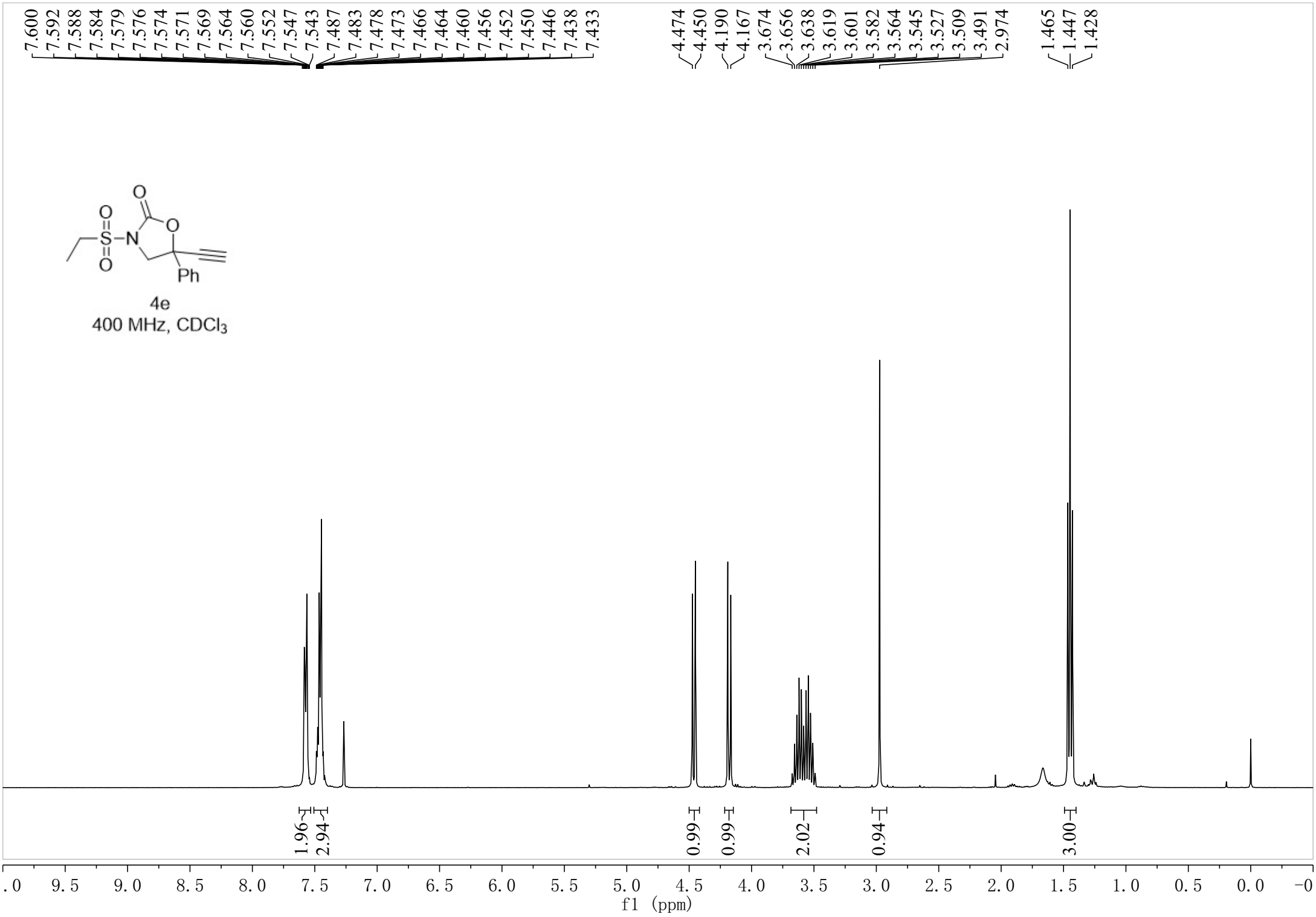
3. (a) Zeng, Q.; Gao, F.; Buchholz, J. B.; Kleij, A. W. *ACS Catal.* **2023**, *13*, 7514–7522. (b) Gómez, J. E.; Cristòfol, À.; Kleij, A. W. *Angew. Chem. Int. Ed.* **2019**, *58*, 3903-3907.
4. (a) Xu, Y.; Hu, X. *Org. Lett.* **2019**, *21*, 8091-8096. (b) Duan, X.; Shi, H.; Yue, Y.; Song, W. *Chem. Commun*. **2024**, *60*, 3926-3929.

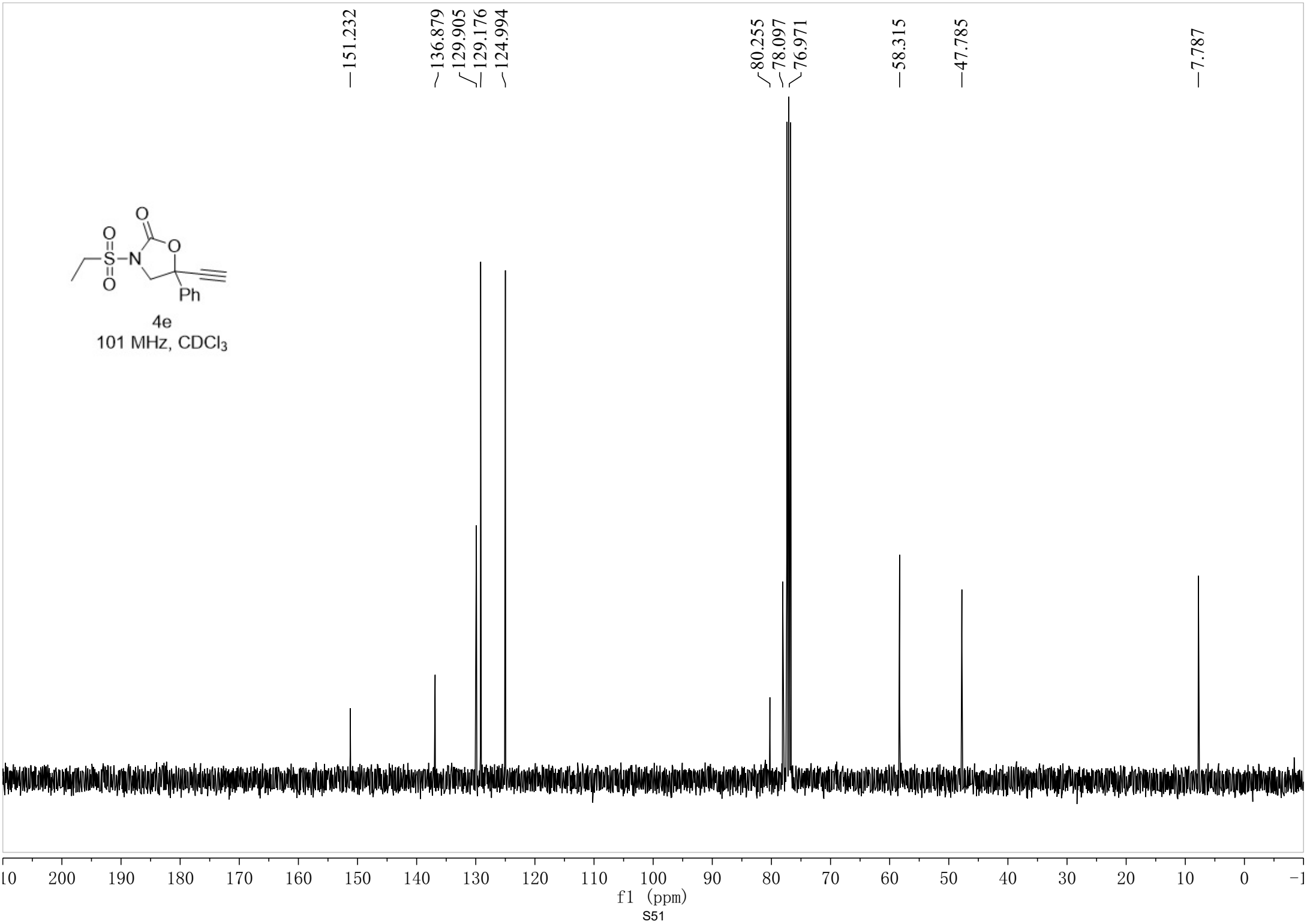

8.344
8.314
7.805
7.775
4.900
4.872
4.515
4.486
3.102
O
O
O
O_2N
2e
300 MHz, $CDCl_3$
2.09
2.09
1.07
1.07
1.00
f1 (ppm)

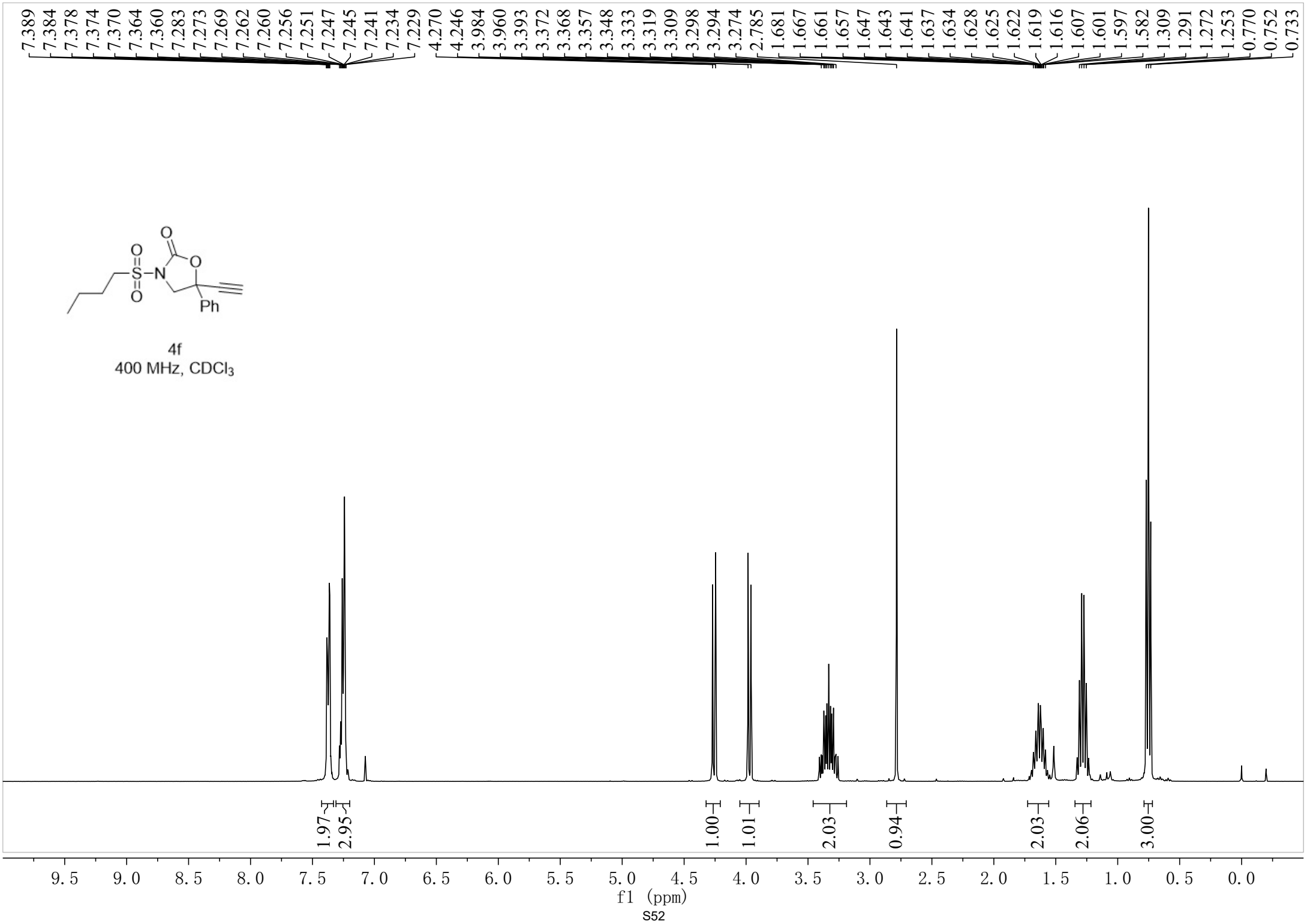

152.77
148.71
143.32
126.33
124.43
79.84
78.79
77.98
76.66
O
O
O
O2N
2e
75 MHz, CDCl3
f1 (ppm)

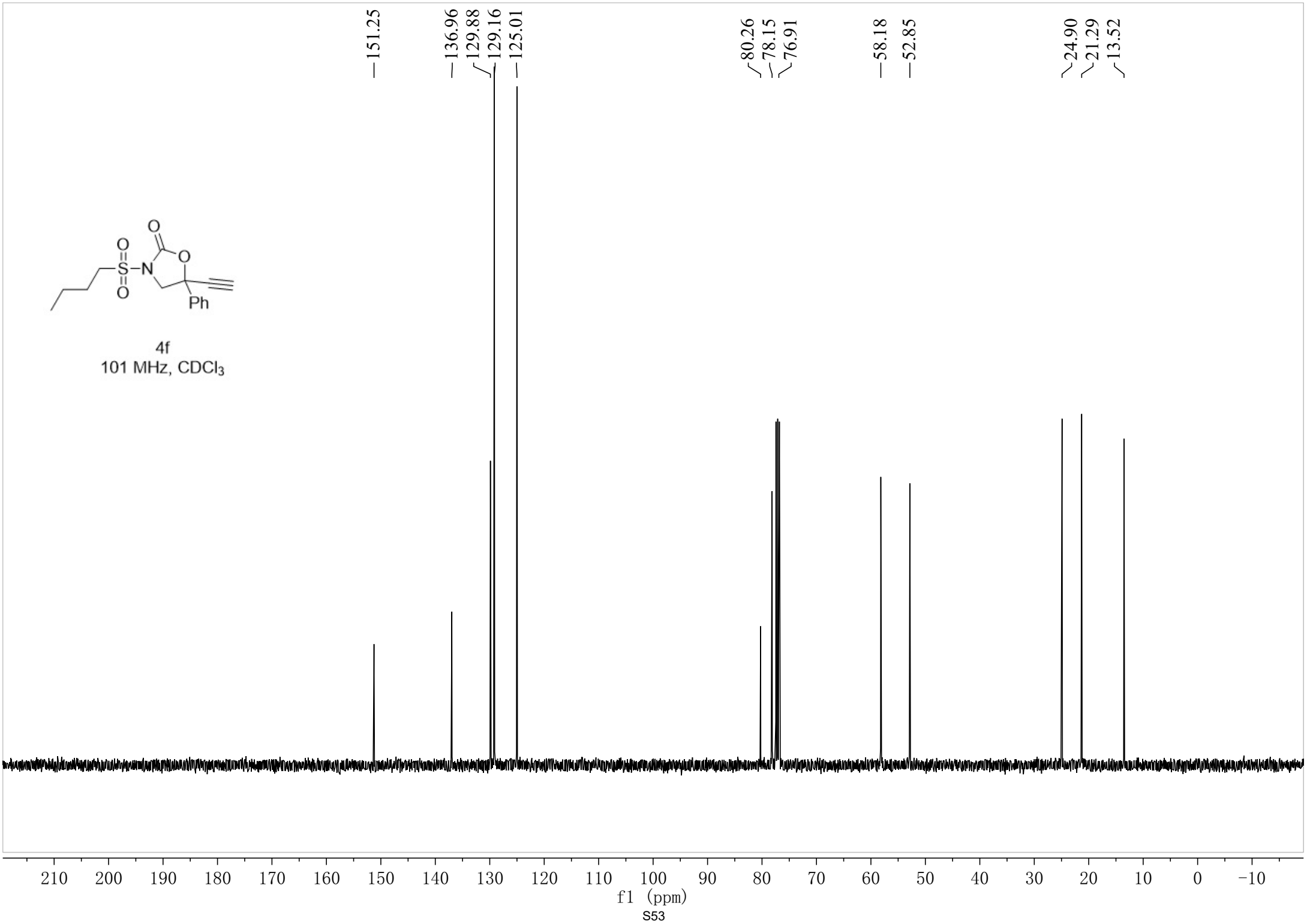

8.631
8.005
8.000
7.980
7.975
7.932
7.906
7.713
7.708
7.690
7.686
7.681
7.664
7.658
7.652
7.647
7.629
7.625
7.620
7.602
7.598
7.458
7.450
7.438
7.425
7.375
7.363
7.351
7.343
7.333
7.327
7.320
7.315
4.571
4.540
4.207
4.175
2.844
O
O
S
N
O
O
O
Ph
4d
300 MHz, CDCl3
1.01
3.05
1.01
2.10
2.05
3.01
1.01
1.02
1.00
f1 (ppm)

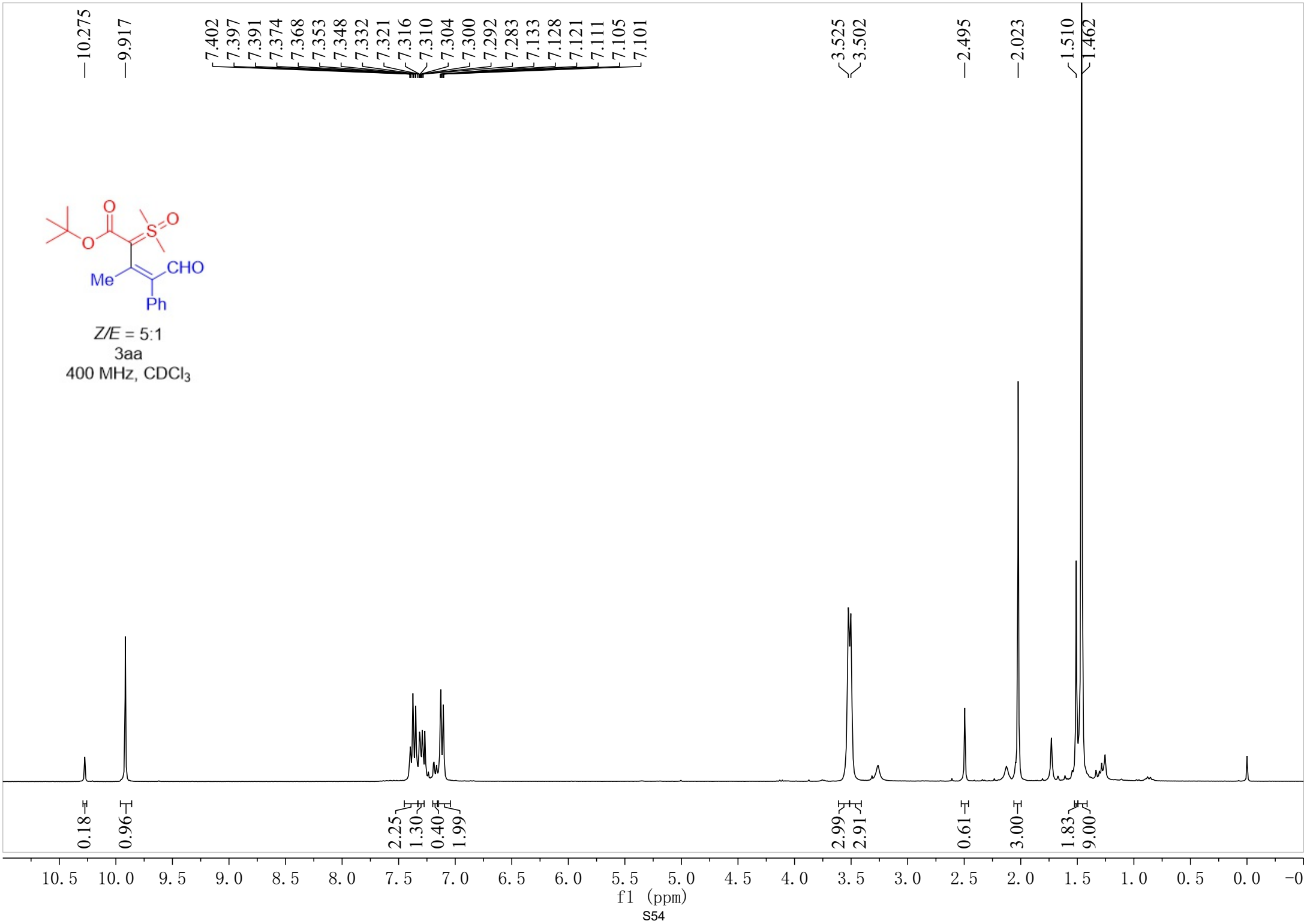

150.43
137.07
135.74
133.61
131.93
130.61
129.89
129.82
129.75
129.07
128.04
127.99
124.95
122.40
80.15
78.09
76.37
58.62
O
O
S
N
O
O
Ph
4d
75 MHz, CDCl3
f1 (ppm)

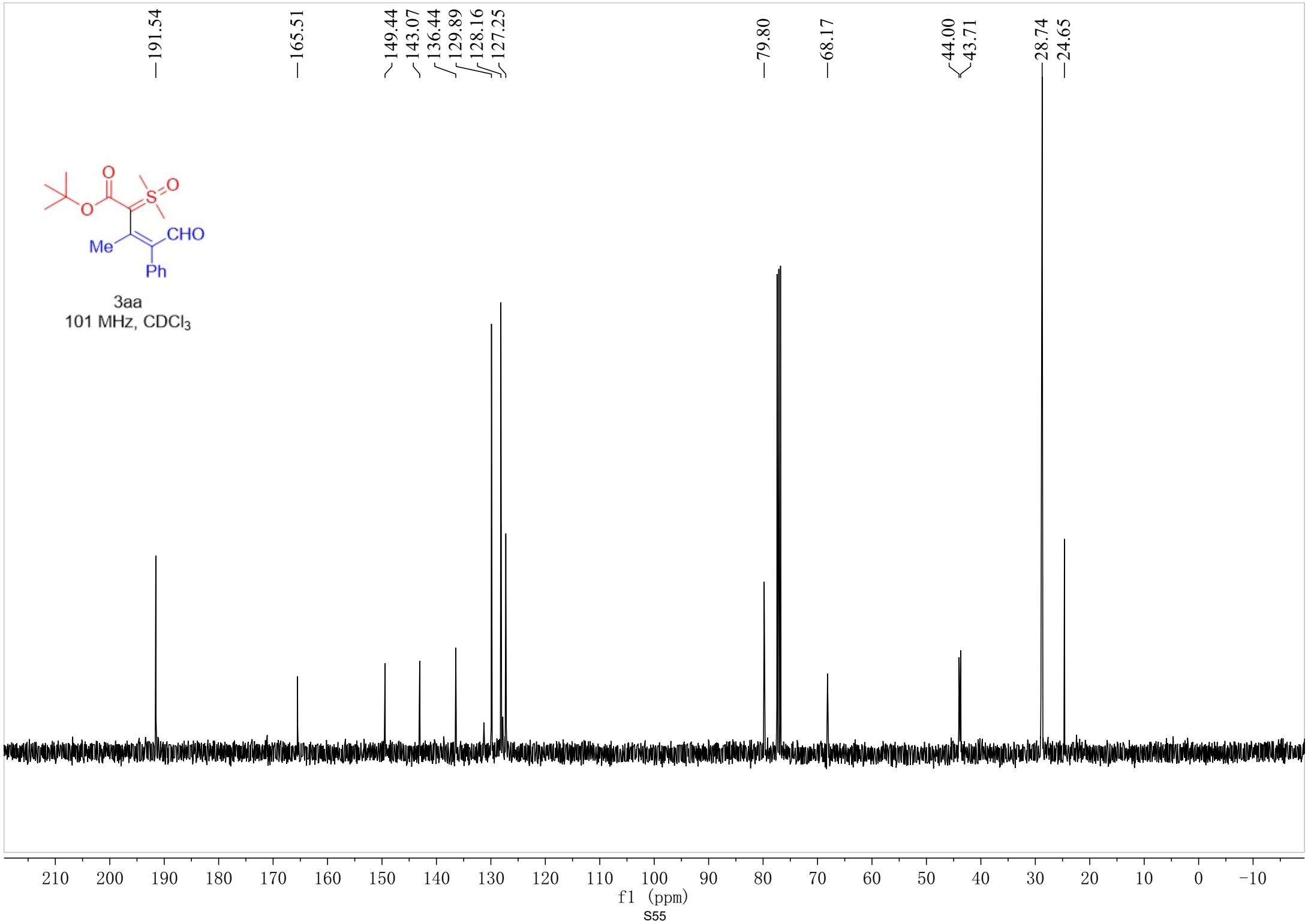

7.600
7.592
7.588
7.584
7.579
7.576
7.574
7.571
7.569
7.564
7.560
7.552
7.547
7.543
7.487
7.483
7.478
7.473
7.466
7.464
7.460
7.456
7.452
7.450
7.446
7.438
7.433
4.474
4.450
4.190
4.167
3.674
3.656
3.638
3.619
3.601
3.582
3.564
3.545
3.527
3.509
3.491
2.974
1.465
1.447
1.428
O
O
S
N
O
O
Ph
4e
400 MHz, CDCl3
1.96
2.94
0.99
0.99
2.02
0.94
3.00
f1 (ppm)

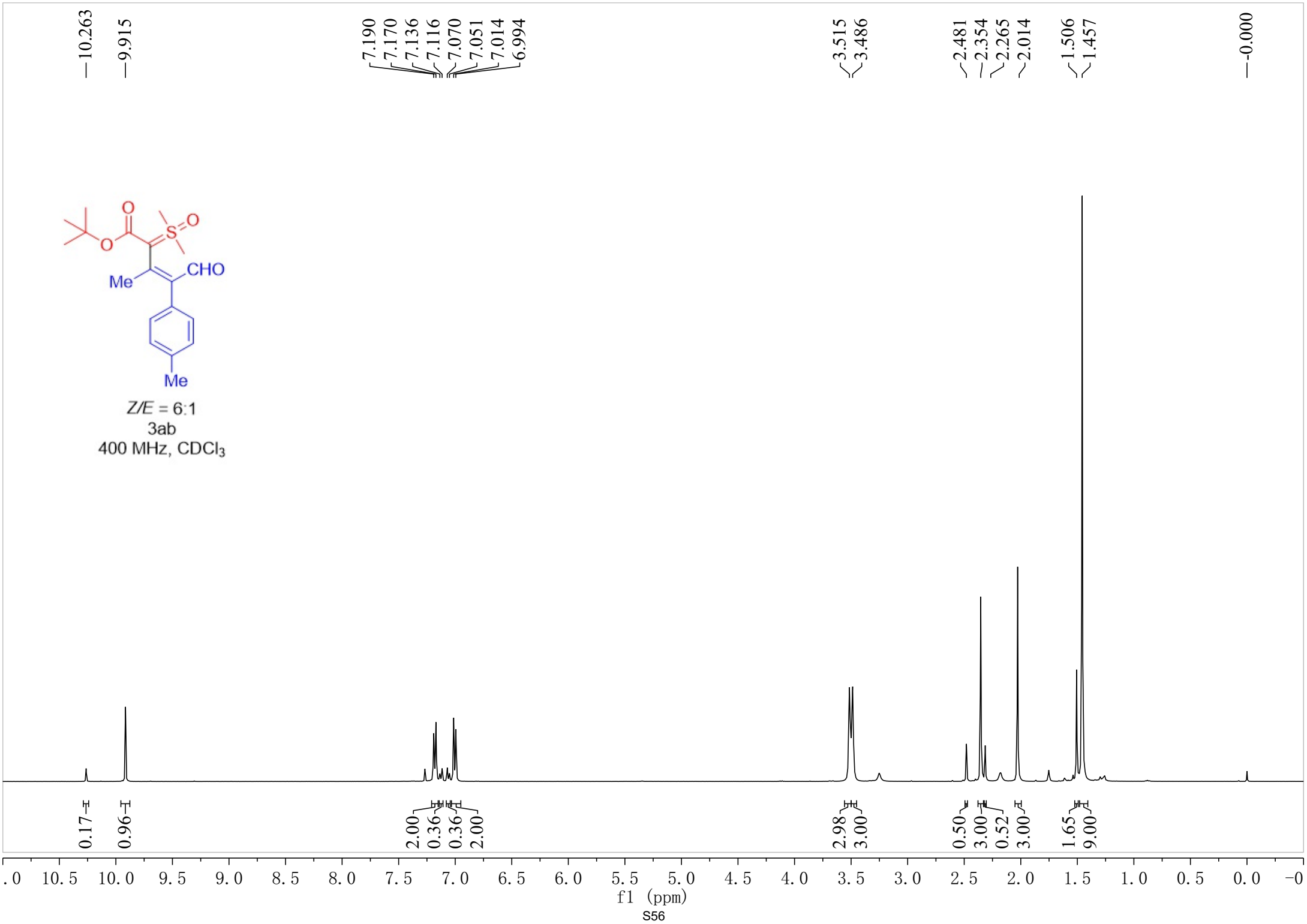

151.232
136.879
129.905
129.176
124.994
80.255
78.097
76.971
58.315
47.785
7.787
4e
101 MHz, CDCl3
f1 (ppm)

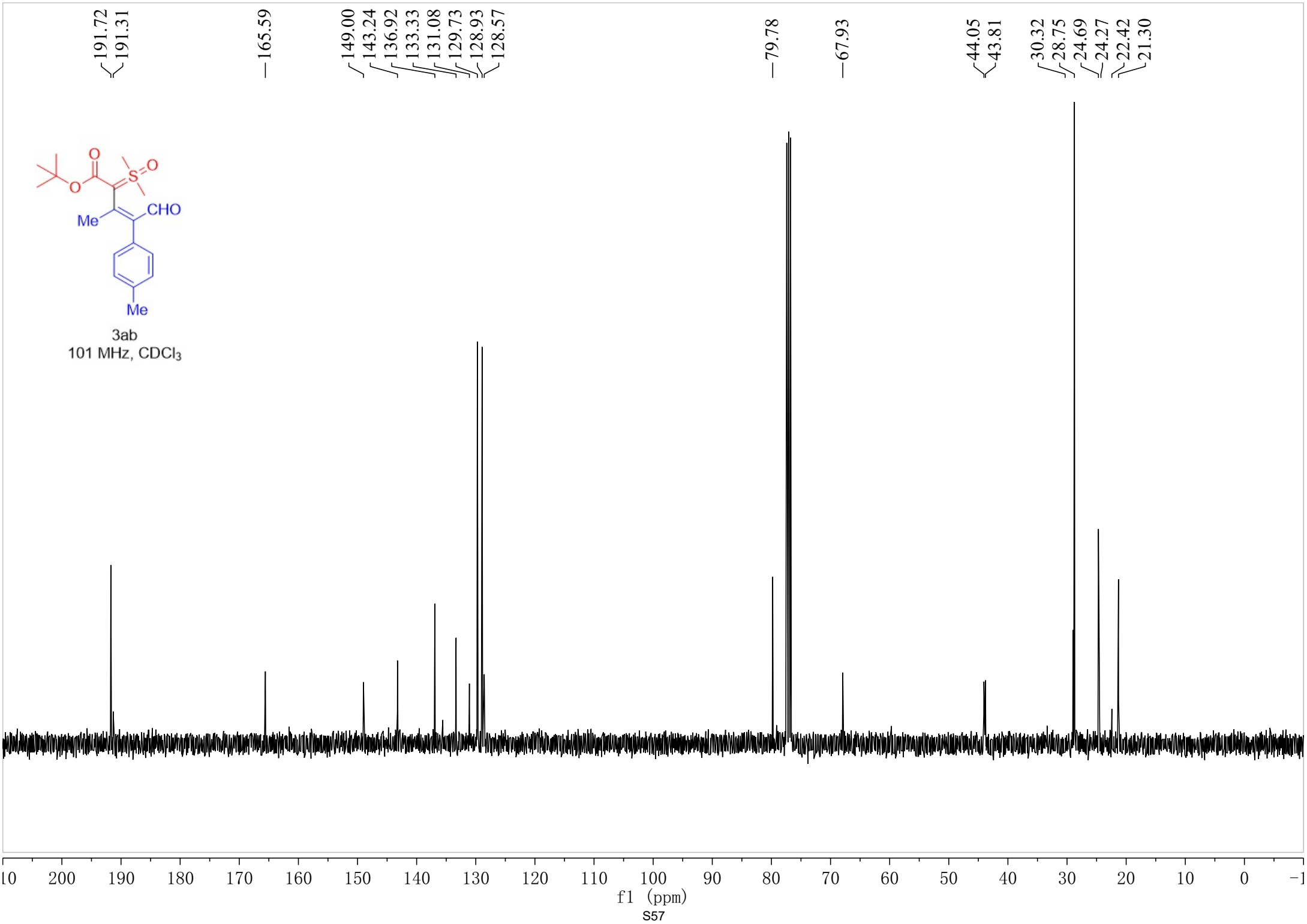

7.389
7.384
7.378
7.374
7.370
7.364
7.360
7.283
7.273
7.269
7.262
7.260
7.256
7.251
7.247
7.245
7.241
7.234
7.229
4.270
4.246
3.984
3.960
3.393
3.372
3.368
3.357
3.348
3.333
3.319
3.309
3.298
3.294
3.274
2.785
1.681
1.667
1.661
1.657
1.647
1.643
1.641
1.637
1.634
1.628
1.625
1.622
1.619
1.616
1.607
1.601
1.597
1.582
1.309
1.291
1.272
1.253
0.770
0.752
0.733
O
O
S
N
O
O
O
Ph
4f
400 MHz, CDCl3
1.97
2.95
1.00
1.01
2.03
0.94
2.03
2.06
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

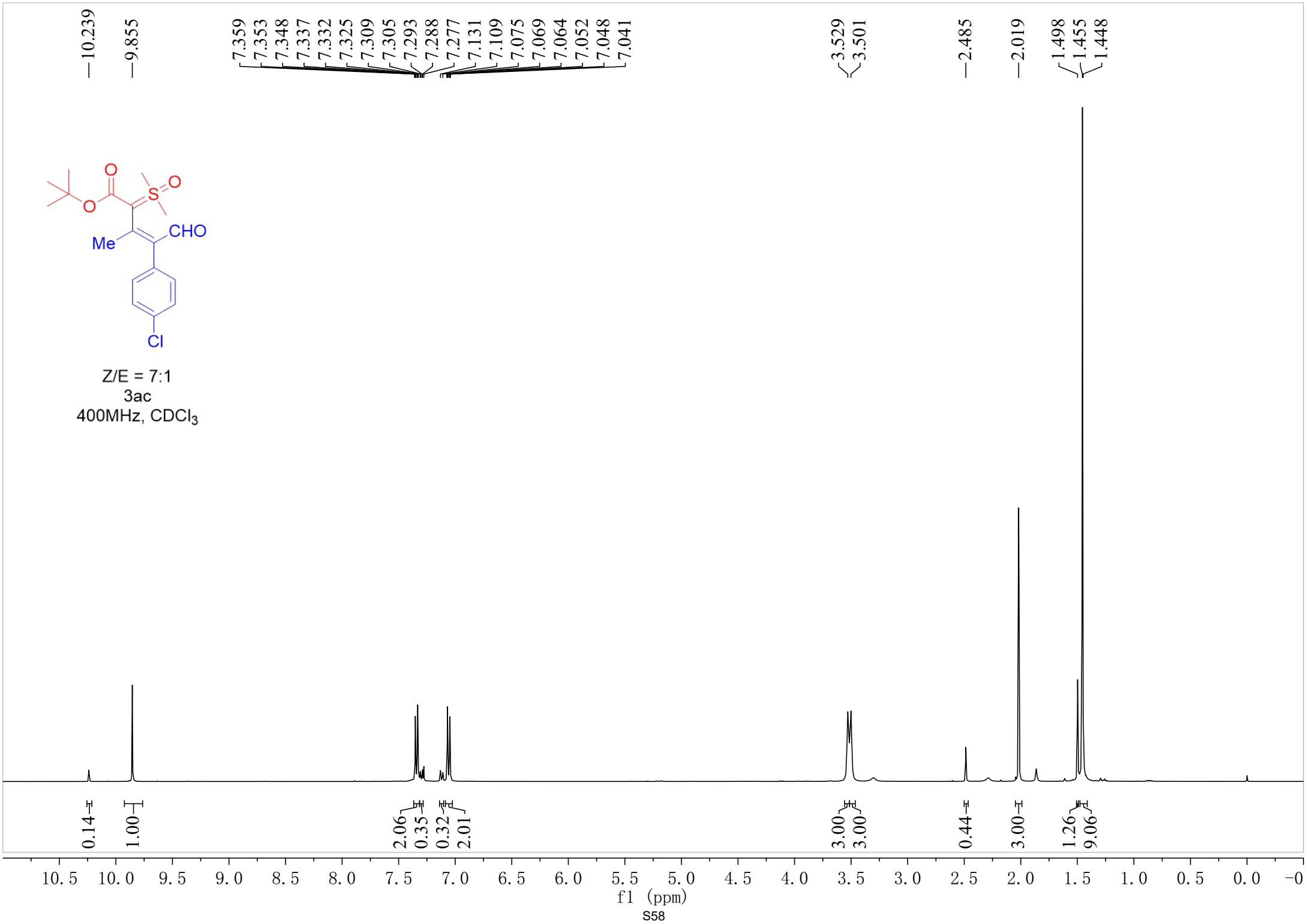

151.25
136.96
129.88
129.16
125.01
80.26
78.15
76.91
58.18
52.85
24.90
21.29
13.52
O
O
S
N
O
O
Ph
4f
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

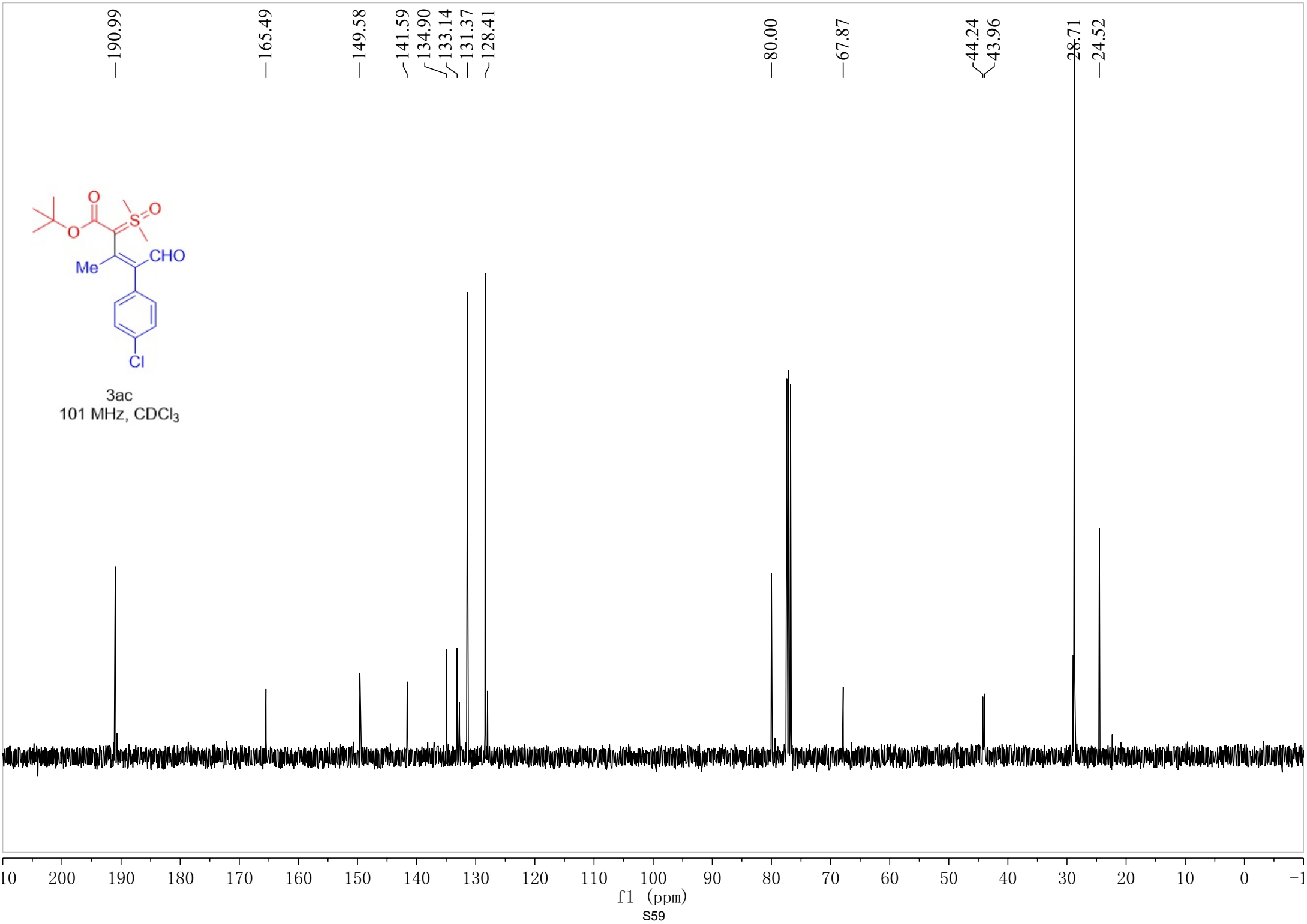

10.275
9.917
7.402
7.397
7.391
7.374
7.368
7.353
7.348
7.332
7.321
7.316
7.310
7.304
7.300
7.292
7.283
7.133
7.128
7.121
7.111
7.105
7.101
3.525
3.502
2.495
2.023
1.510
1.462
O
O
S
O
Me
CHO
Ph
Z/E = 5:1
3aa
400 MHz, CDCl3
0.18
0.96
2.25
1.30
0.40
1.99
2.99
2.91
0.61
3.00
1.83
9.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

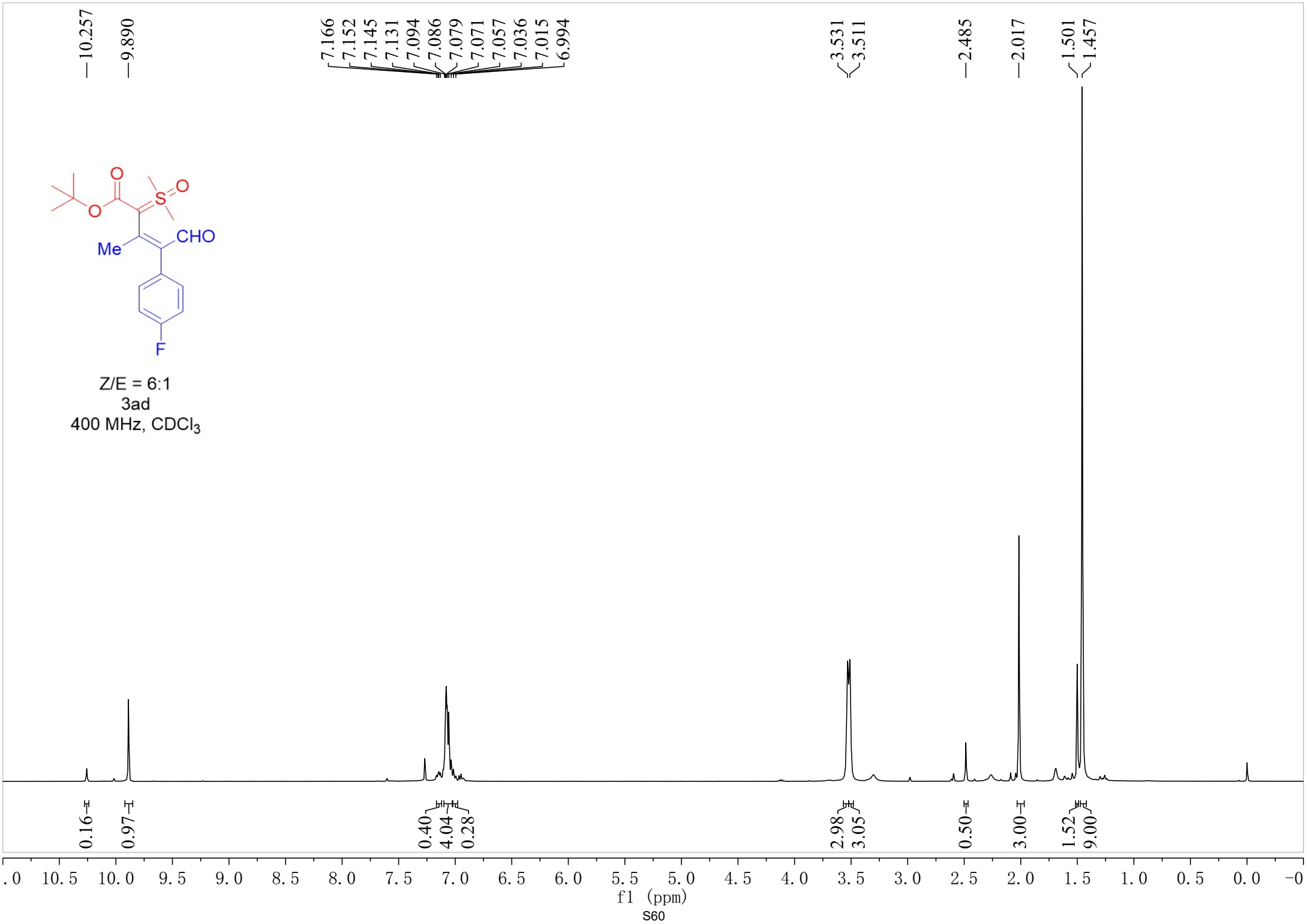

191.54
165.51
149.44
143.07
136.44
129.89
128.16
127.25
79.80
68.17
44.00
43.71
28.74
24.65
O
O
S
O
Me
CHO
Ph
3aa
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

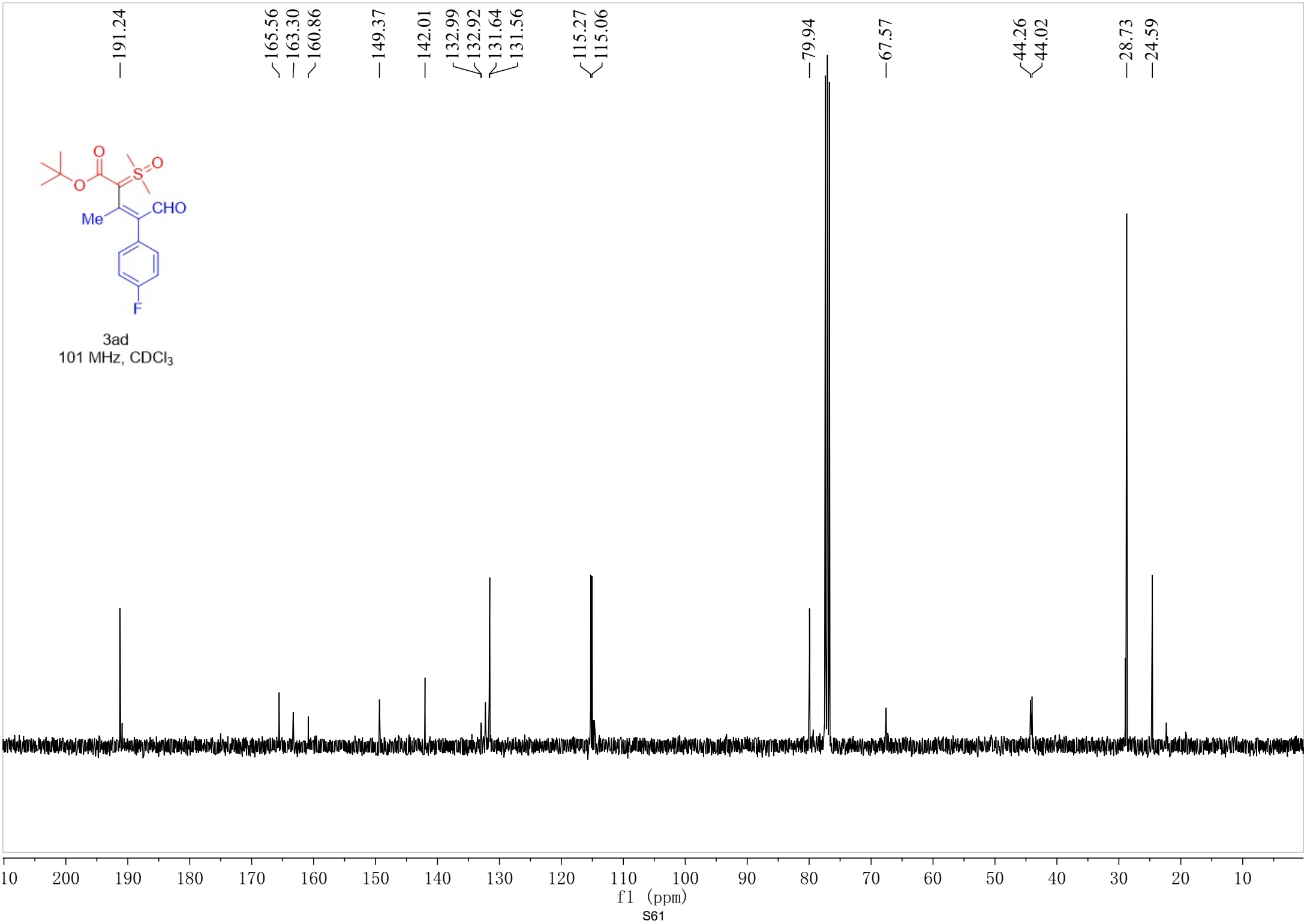

10.263
9.915
7.190
7.170
7.136
7.116
7.070
7.051
7.014
6.994
3.515
3.486
2.481
2.354
2.265
2.014
1.506
1.457
-0.000
O
O
S
O
Me
CHO
Me
Z/E = 6:1
3ab
400 MHz, CDCl3
0.17
0.96
2.00
0.36
0.36
2.00
2.98
3.00
0.50
3.00
0.52
3.00
1.65
9.00
f1 (ppm)

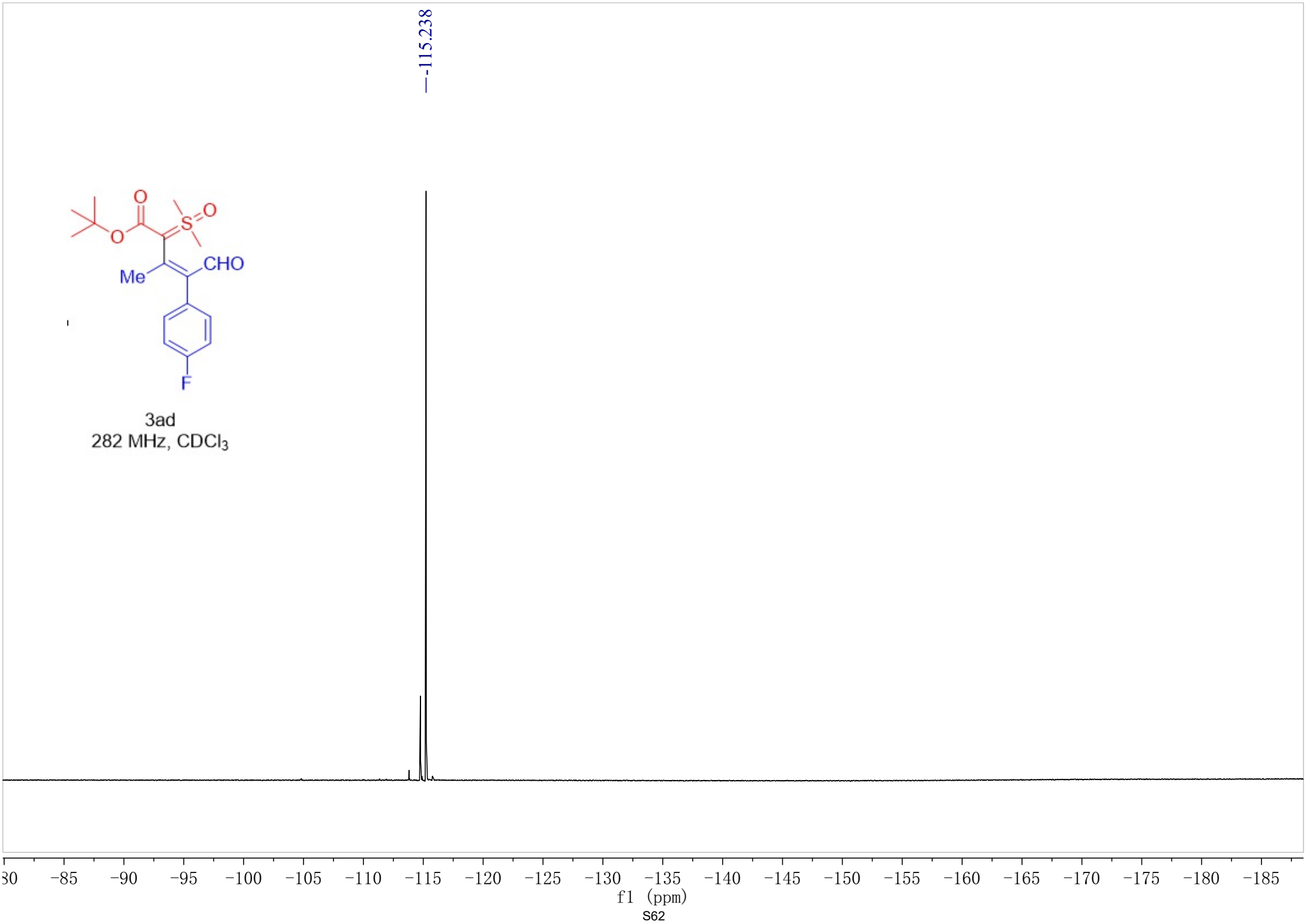

191.72
191.31
165.59
149.00
143.24
136.92
133.33
131.08
129.73
128.93
128.57
79.78
67.93
44.05
43.81
30.32
28.75
24.69
24.27
22.42
21.30
O
O
S
O
Me
CHO
Me
3ab
101 MHz, CDCl3
f1 (ppm)


10.239
9.855
7.359
7.353
7.348
7.337
7.332
7.325
7.309
7.305
7.293
7.288
7.277
7.131
7.109
7.075
7.069
7.064
7.052
7.048
7.041
3.529
3.501
2.485
2.019
1.498
1.455
1.448
O
O
S
O
Me
CHO
Cl
Z/E = 7:1
3ac
400MHz, CDCl3
0.14
1.00
2.06
0.35
0.32
2.01
3.00
3.00
0.44
3.00
1.26
9.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)


190.99
165.49
149.58
141.59
134.90
133.14
131.37
128.41
80.00
67.87
44.24
43.96
28.71
24.52
O
O
S
O
Me
CHO
Cl
3ac
101 MHz, CDCl3
f1 (ppm)


10.257
9.890
7.166
7.152
7.145
7.131
7.094
7.086
7.079
7.071
7.057
7.036
7.015
6.994
3.531
3.511
2.485
2.017
1.501
1.457
O
O
S
O
Me
CHO
F
Z/E = 6:1
3ad
400 MHz, CDCl3
0.16
0.97
0.40
4.04
0.28
2.98
3.05
0.50
3.00
1.52
9.00
f1 (ppm)


191.24
165.56
163.30
160.86
149.37
142.01
132.99
132.92
131.64
131.56
115.27
115.06
79.94
67.57
44.26
44.02
28.73
24.59
O
O
S
O
Me
CHO
F
3ad
101 MHz, CDCl3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


-115.238
O
O
S
O
Me
CHO
F
3ad
282 MHz, CDCl3
30
-85
-90
-95
-100
-105
-110
-115
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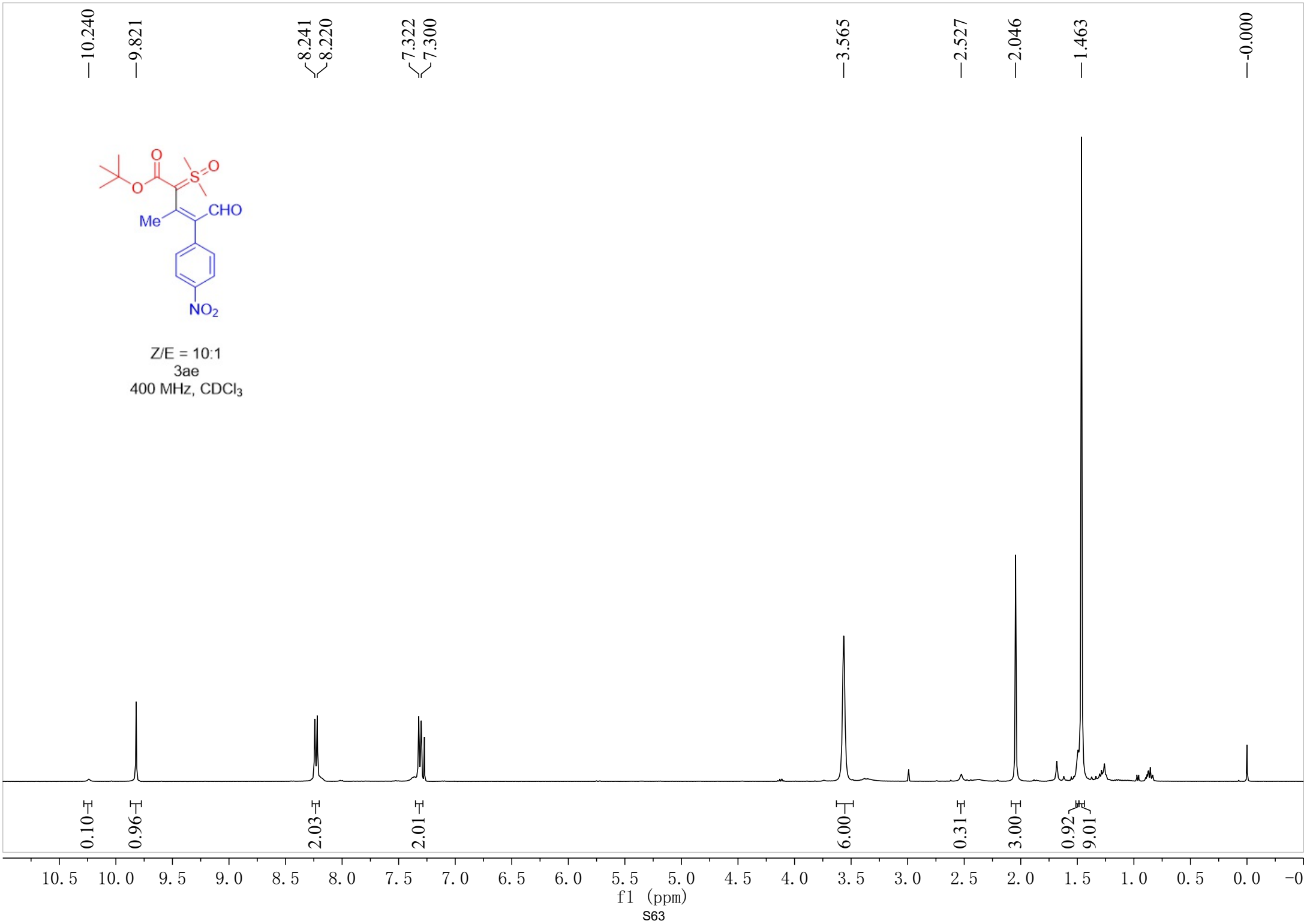
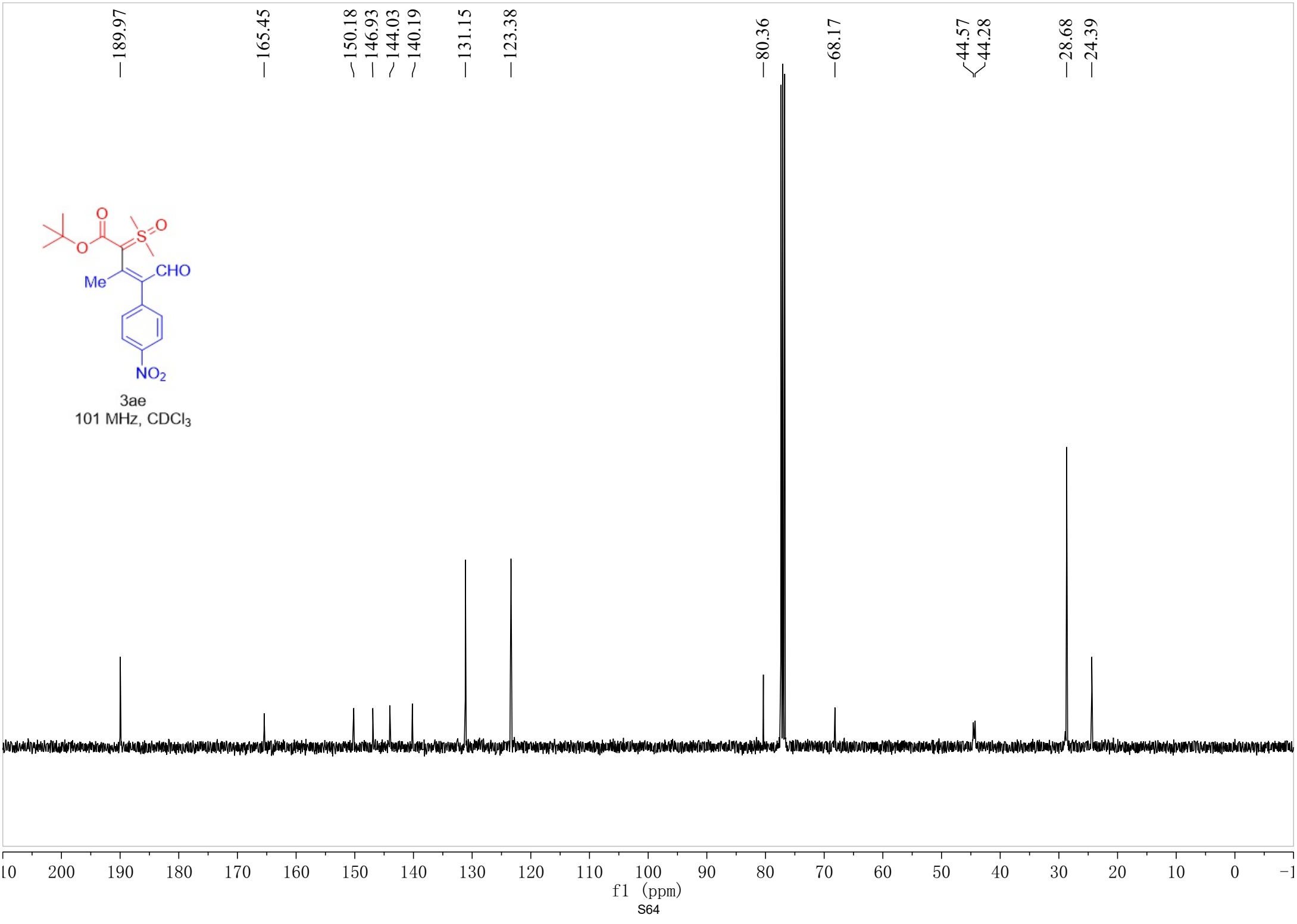
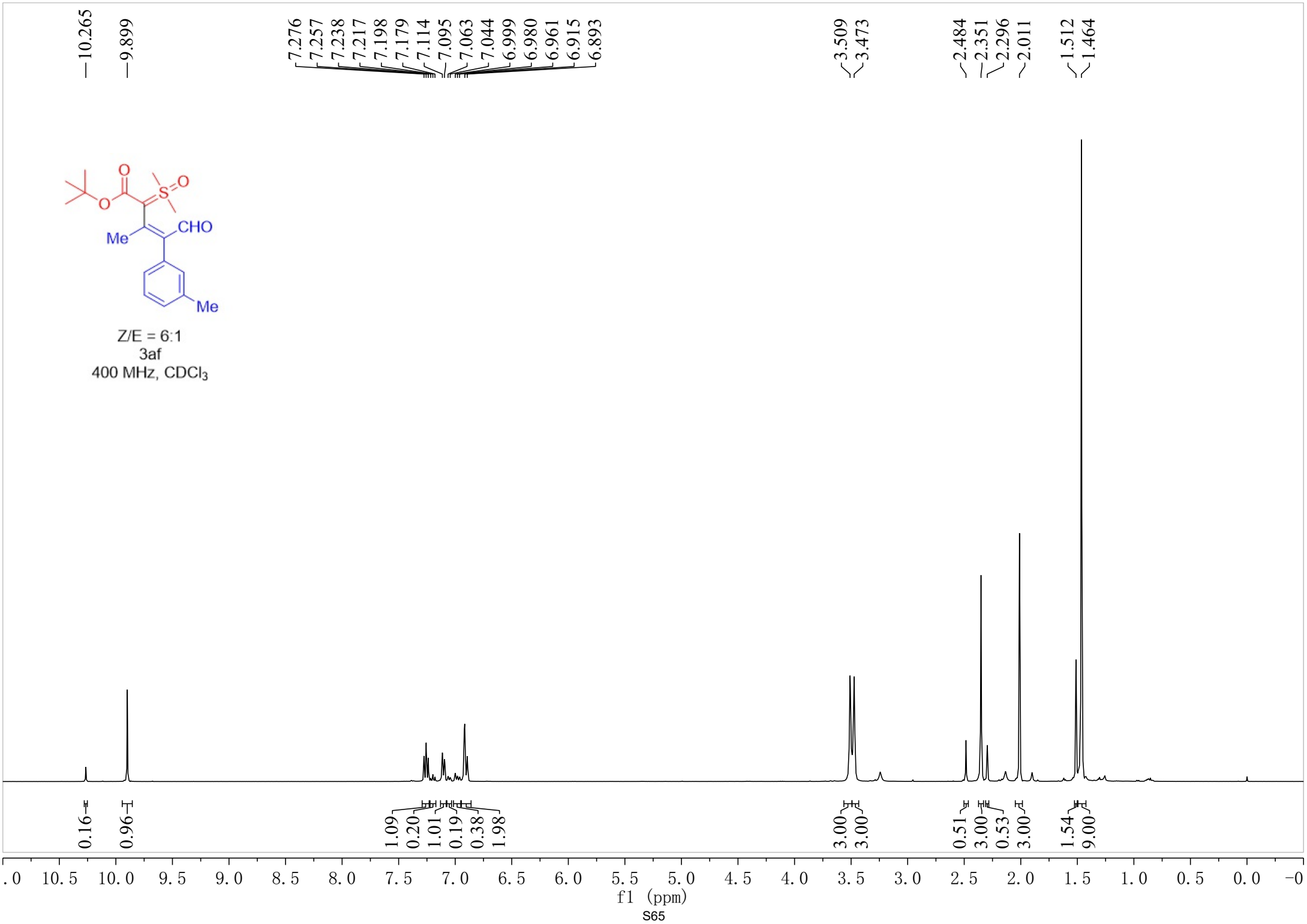
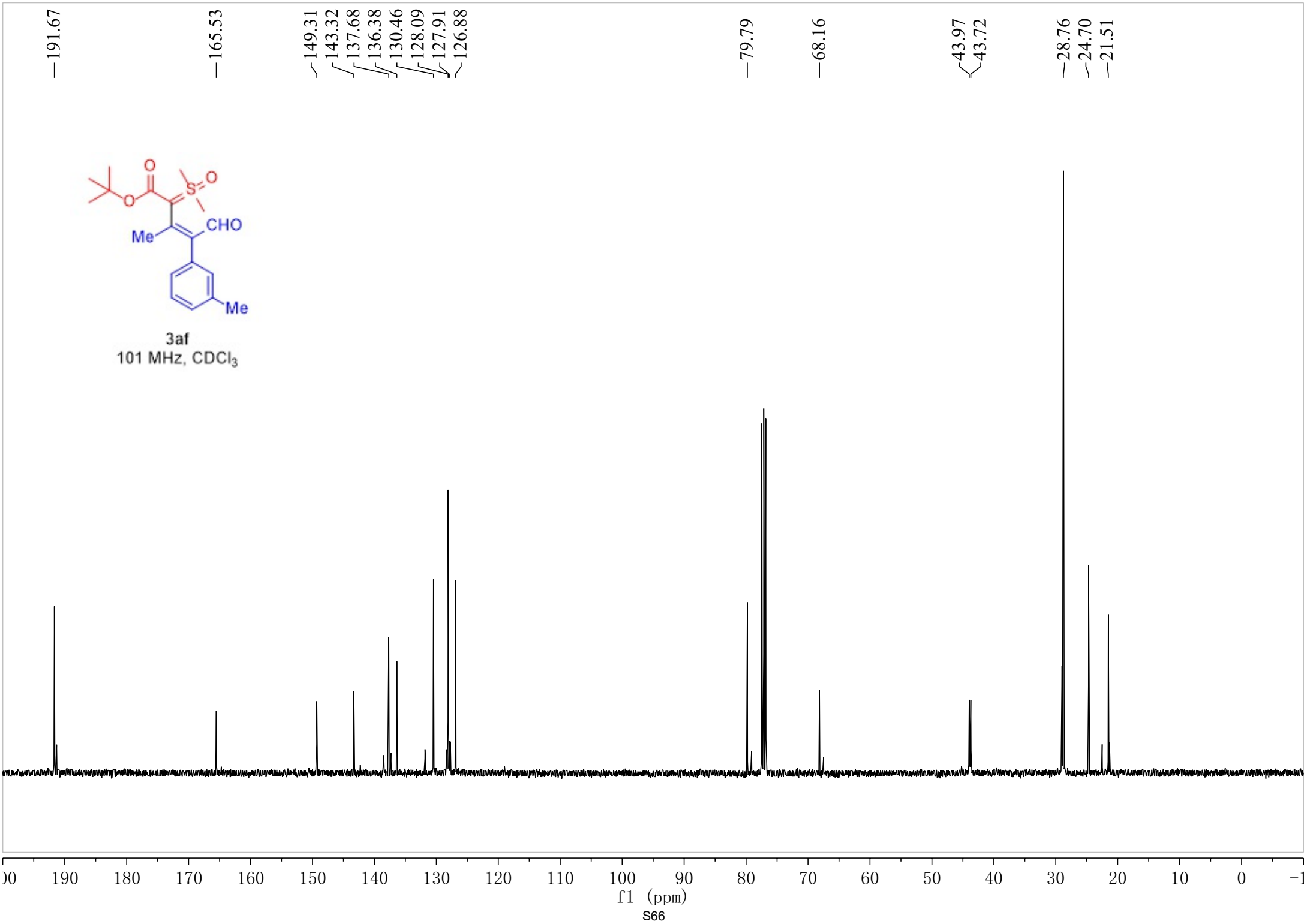
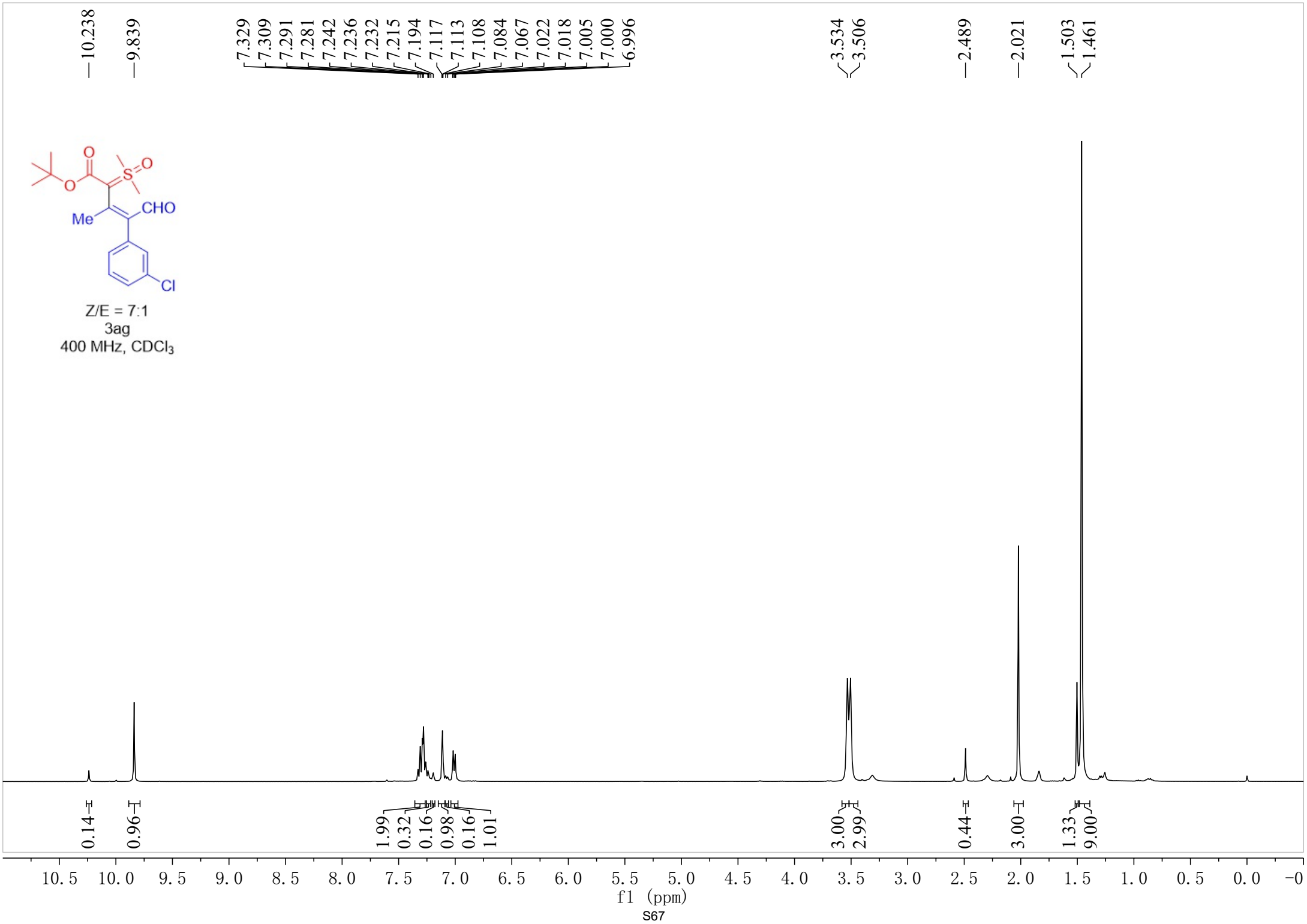
-165
-170
-175
-180
-185
f1 (ppm)

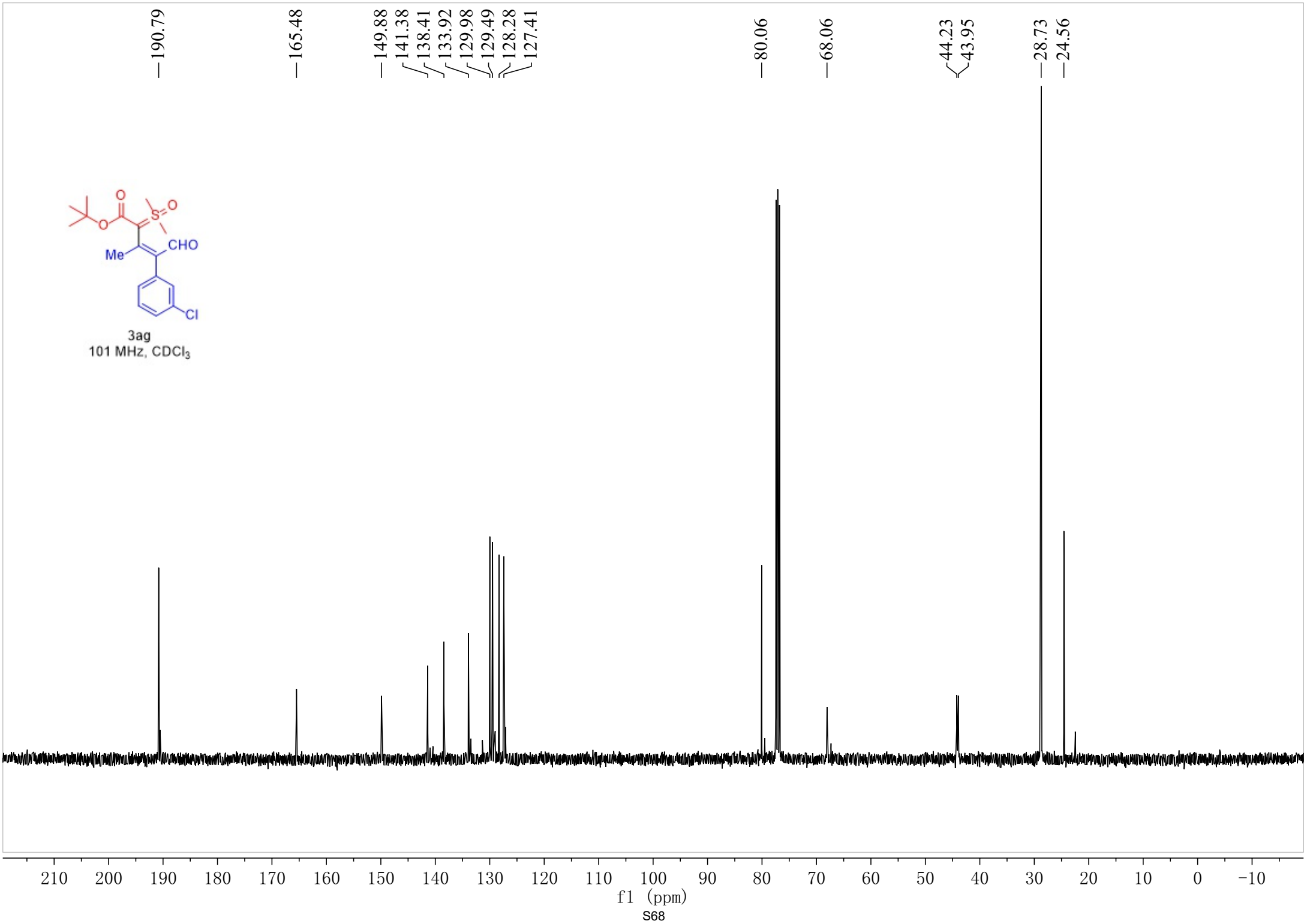

10.240
9.821
8.241
8.220
7.322
7.300
3.565
2.527
2.046
1.463
-0.000
Me
CHO
NO2
Z/E = 10:1
3ae
400 MHz, CDCl3
0.10
0.96
2.03
2.01
6.00
0.31
3.00
0.92
9.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

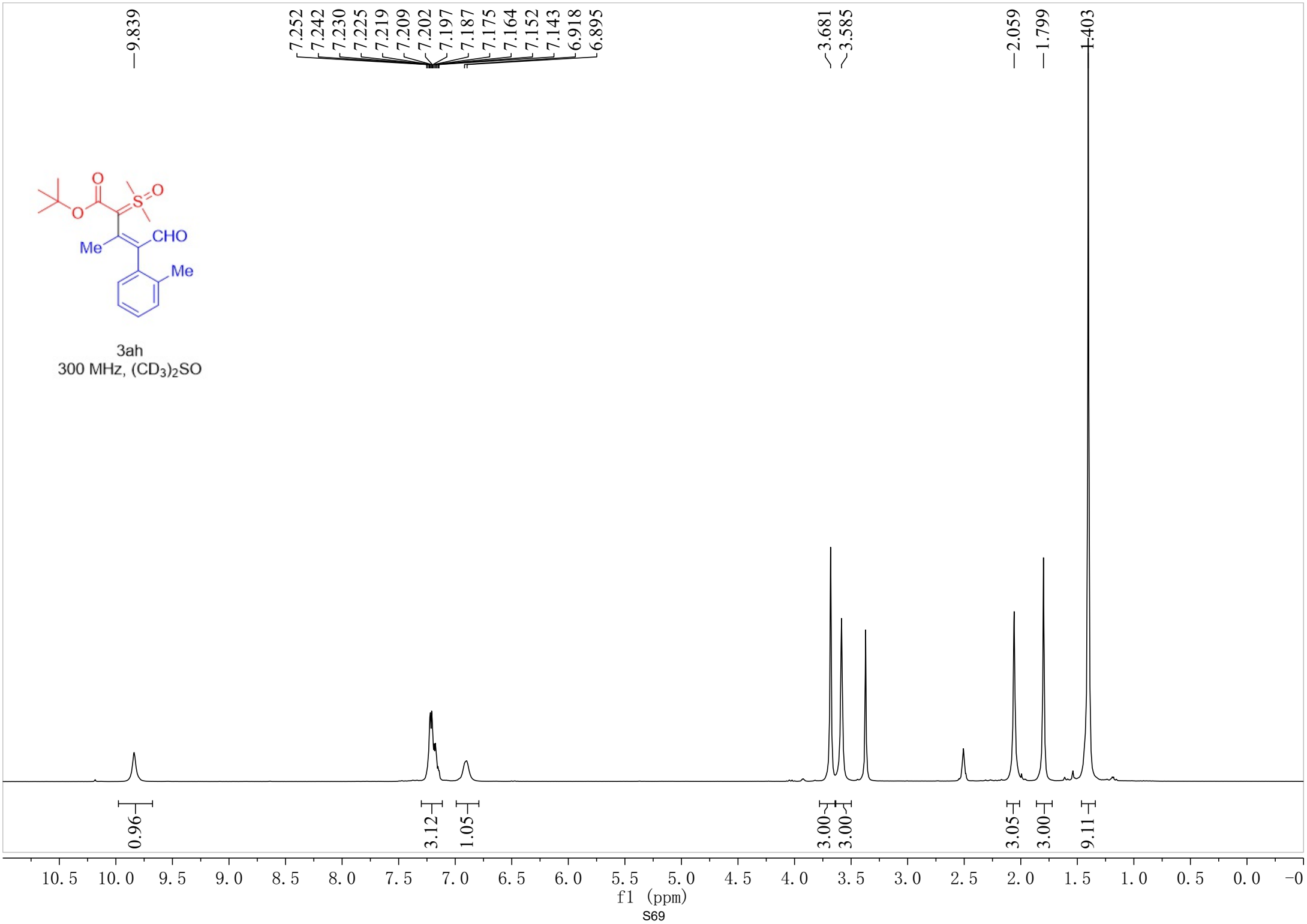

189.97
165.45
150.18
146.93
144.03
140.19
131.15
123.38
80.36
68.17
44.57
44.28
28.68
24.39
O
O
S
O
Me
CHO
NO2
3ae
101 MHz, CDCl3
f1 (ppm)

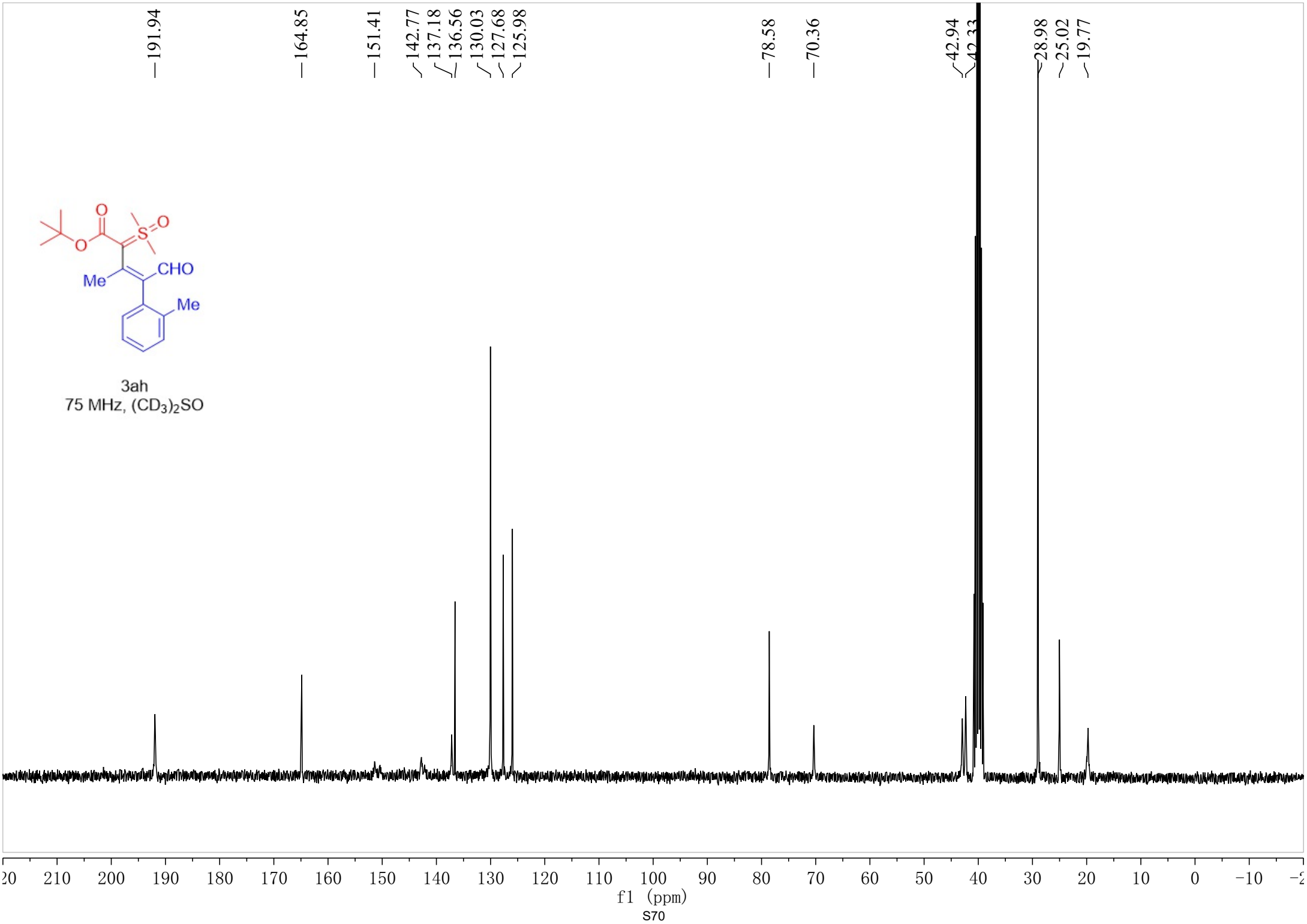

10.265
9.899
7.276
7.257
7.238
7.217
7.198
7.179
7.114
7.095
7.063
7.044
6.999
6.980
6.961
6.915
6.893
3.509
3.473
2.484
2.351
2.296
2.011
1.512
1.464
Me
CHO
Me
Z/E = 6:1
3af
400 MHz, CDCl3
0.16
0.96
1.09
0.20
1.01
0.19
0.38
1.98
3.00
3.00
0.51
3.00
0.53
3.00
1.54
9.00
f1 (ppm)

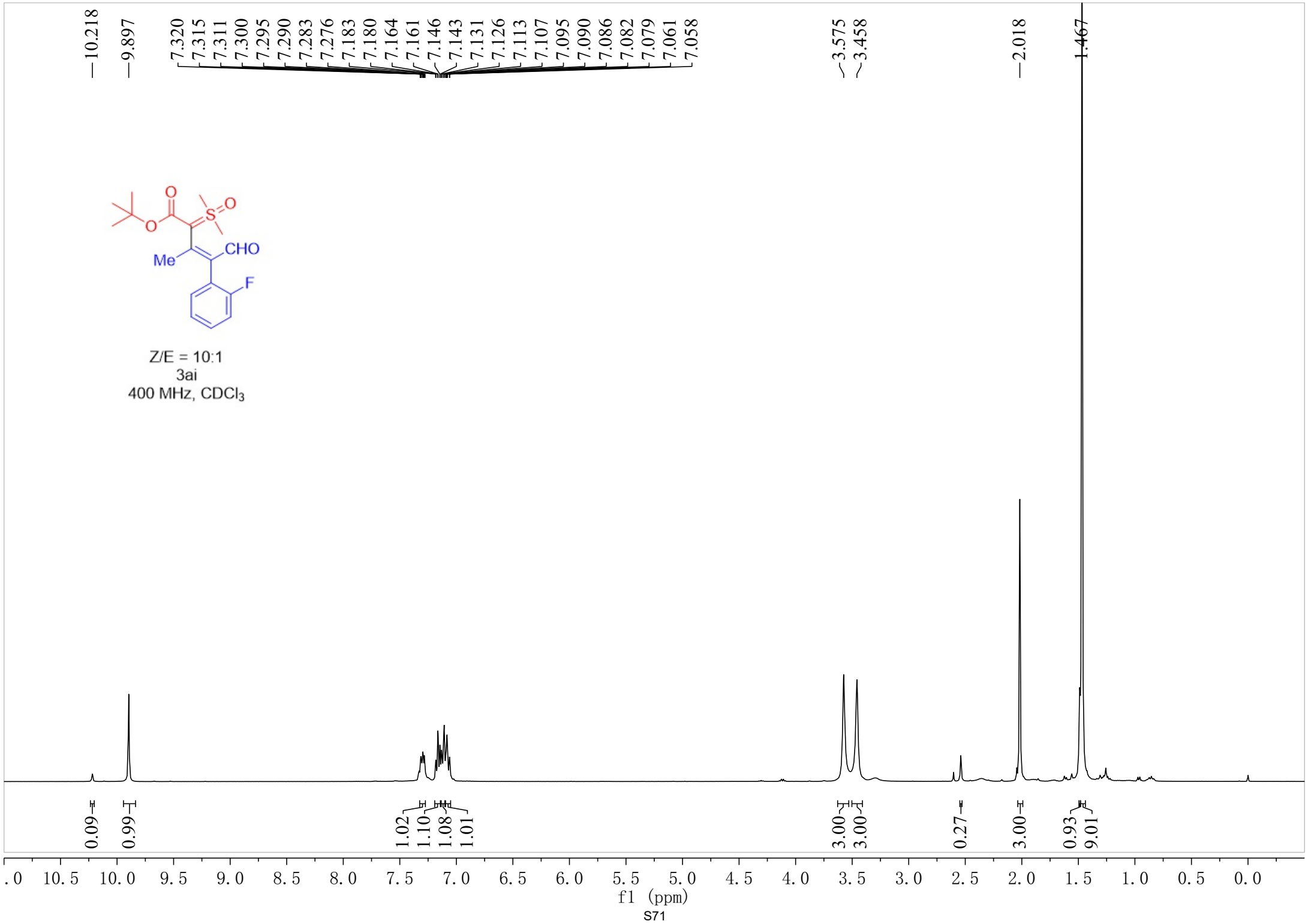

191.67
165.53
149.31
143.32
137.68
136.38
130.46
128.09
127.91
126.88
79.79
68.16
43.97
43.72
28.76
24.70
21.51
O
O
S
O
Me
CHO
Me
3af
101 MHz, CDCl3
f1 (ppm)

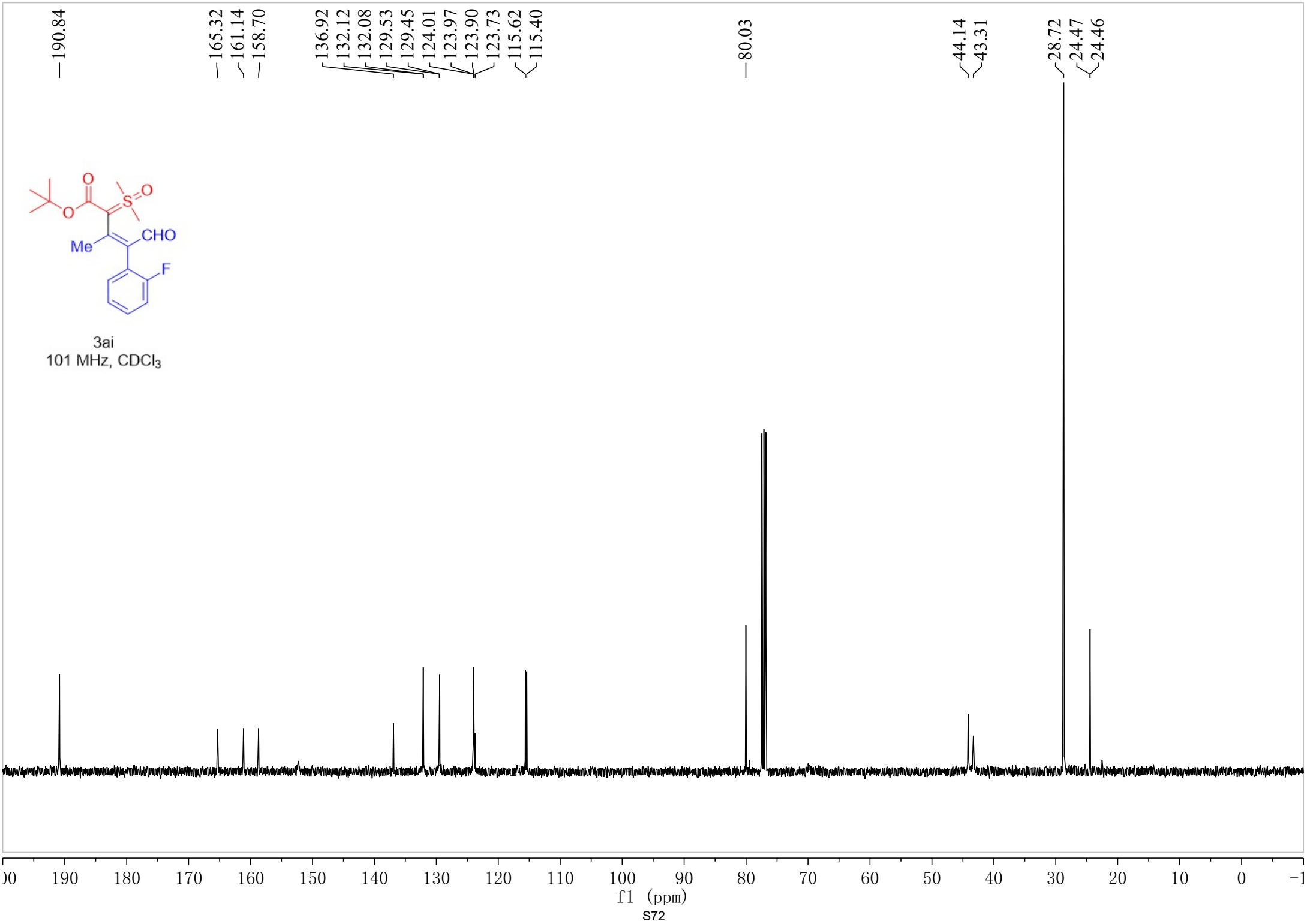

10.238
9.839
7.329
7.309
7.291
7.281
7.242
7.236
7.232
7.215
7.194
7.117
7.113
7.108
7.084
7.067
7.022
7.018
7.005
7.000
6.996
3.534
3.506
2.489
2.021
1.503
1.461
Me
CHO
Cl
Z/E = 7:1
3ag
400 MHz, CDCl3
0.14
0.96
1.99
0.32
0.16
0.98
0.16
1.01
3.00
2.99
0.44
3.00
1.33
9.00
f1 (ppm)


190.79
165.48
149.88
141.38
138.41
133.92
129.98
129.49
128.28
127.41
80.06
68.06
44.23
43.95
28.73
24.56
O
O
S
O
Me
CHO
Cl
3ag
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

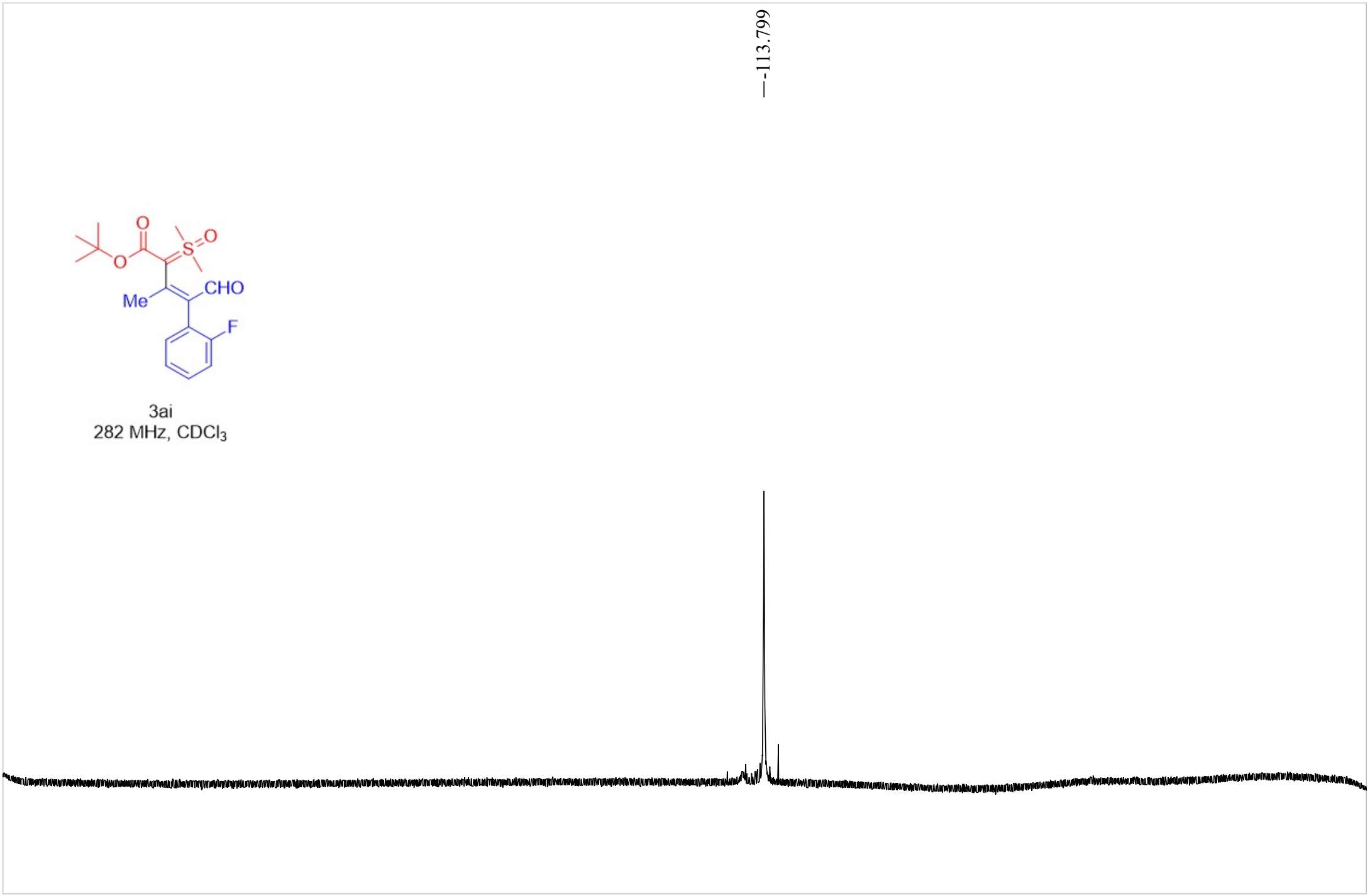

9.839
7.252
7.242
7.230
7.225
7.219
7.209
7.202
7.197
7.187
7.175
7.164
7.152
7.143
6.918
6.895
3.681
3.585
2.059
1.799
1.403
O
O
S
O
Me
CHO
Me
3ah
300 MHz, (CD3)2SO
0.96
3.12
1.05
3.00
3.00
3.05
3.00
9.11
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0
f1 (ppm)

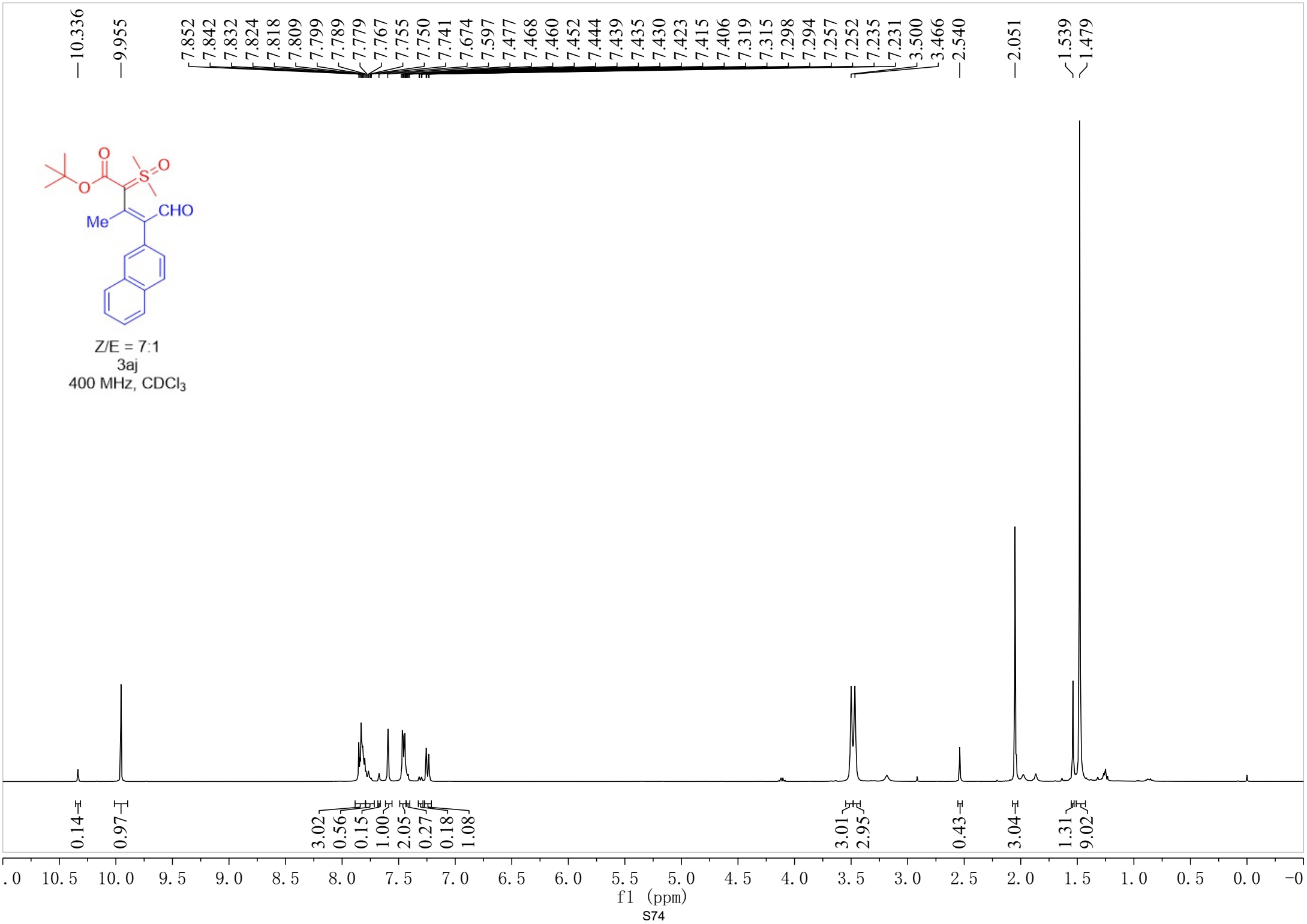

191.94
164.85
151.41
142.77
137.18
136.56
130.03
127.68
125.98
78.58
70.36
42.94
42.33
28.98
25.02
19.77
O
O
S
O
Me
CHO
Me
3ah
75 MHz, (CD3)2SO
f1 (ppm)

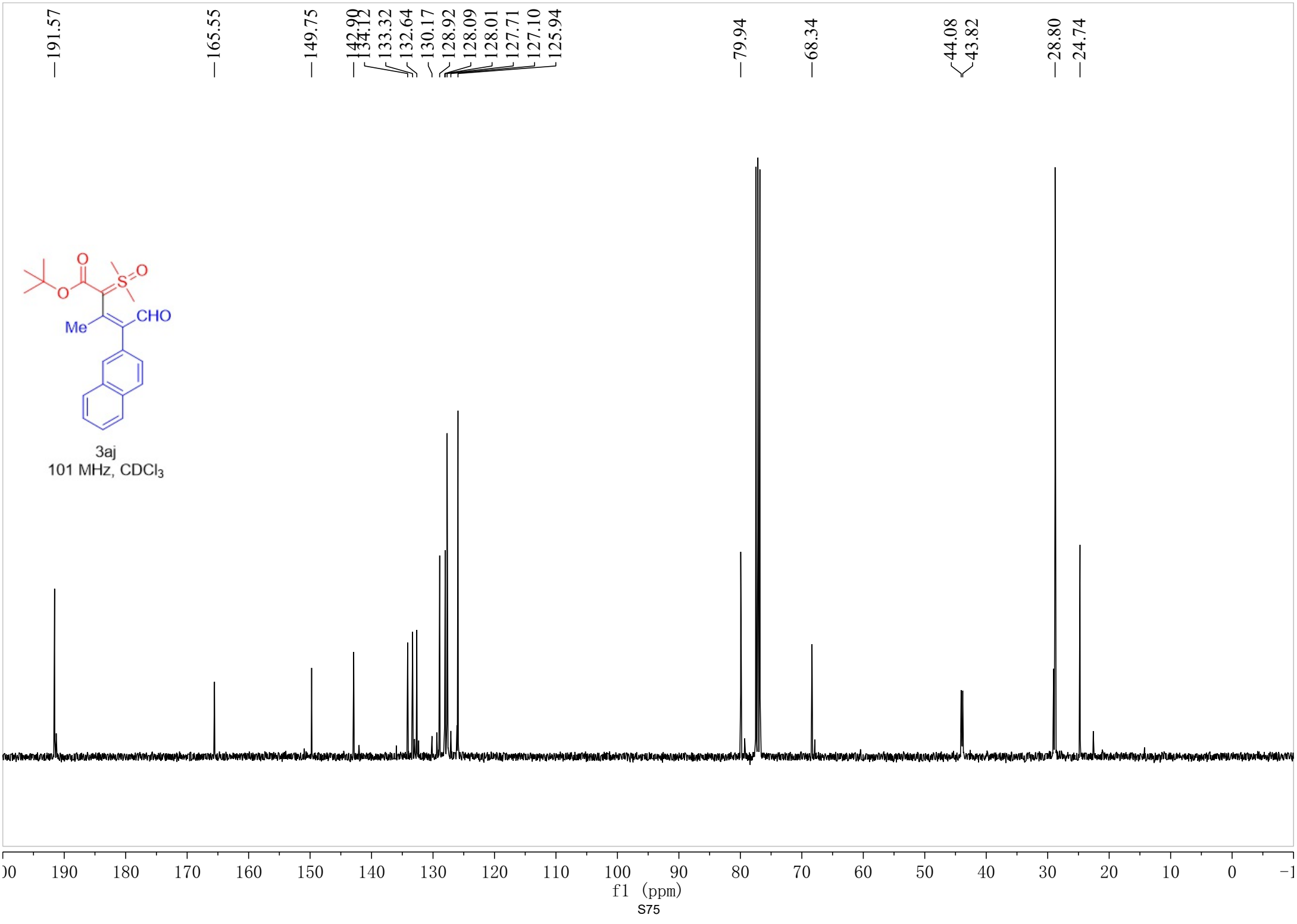

10.218
9.897
7.320
7.315
7.311
7.300
7.295
7.290
7.283
7.276
7.183
7.180
7.164
7.161
7.146
7.143
7.131
7.126
7.113
7.107
7.095
7.090
7.086
7.082
7.079
7.061
7.058
3.575
3.458
2.018
1.467
O
O
S
O
Me
CHO
F
Z/E = 10:1
3ai
400 MHz, CDCl3
0.09
0.99
1.02
1.10
1.08
1.01
3.00
3.00
0.27
3.00
0.93
9.01
f1 (ppm)

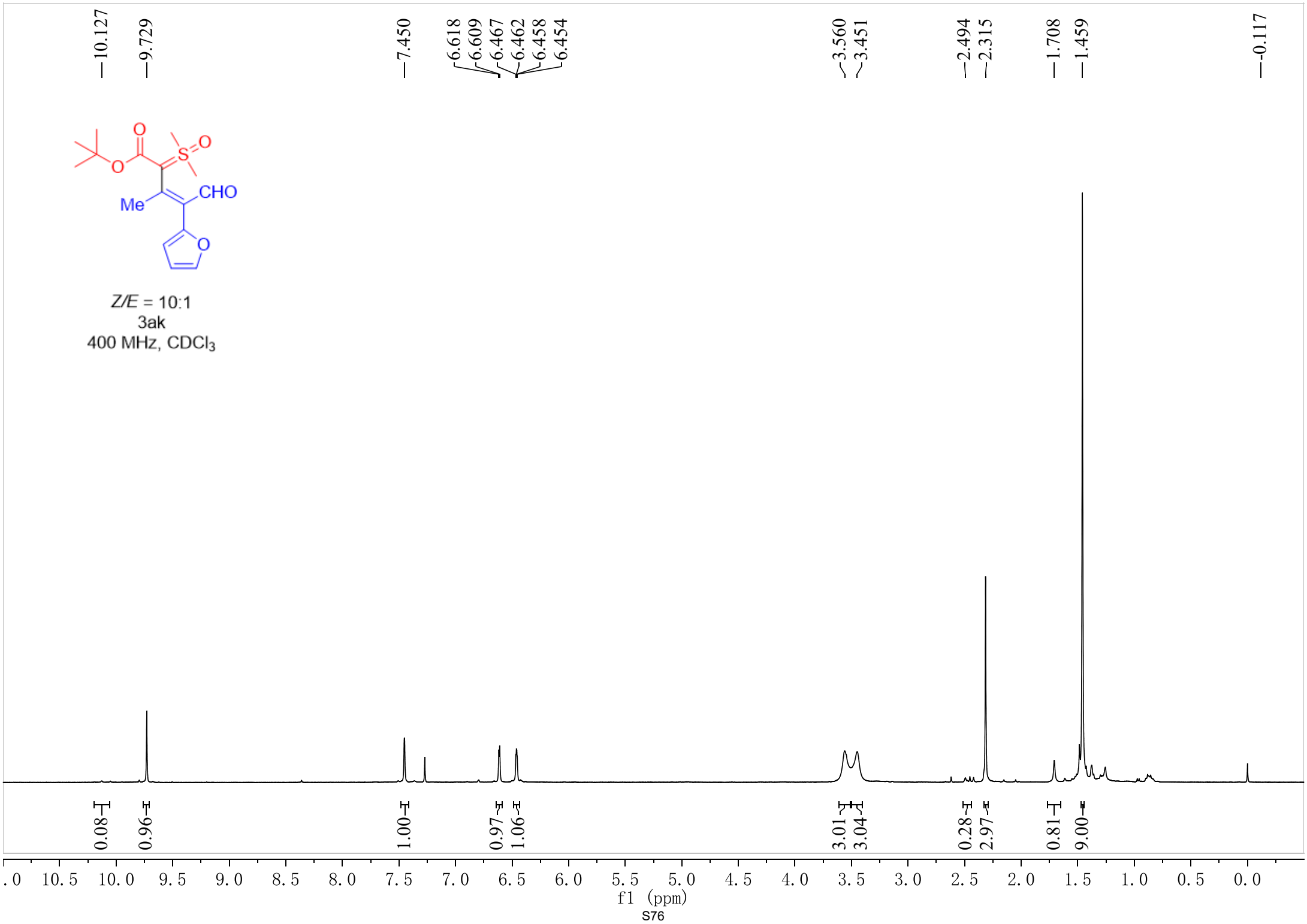

190.84
165.32
161.14
158.70
136.92
132.12
132.08
129.53
129.45
124.01
123.97
123.90
123.73
115.62
115.40
80.03
44.14
43.31
28.72
24.47
24.46
O
O
S=O
Me
CHO
F
3ai
101 MHz, CDCl3
f1 (ppm)

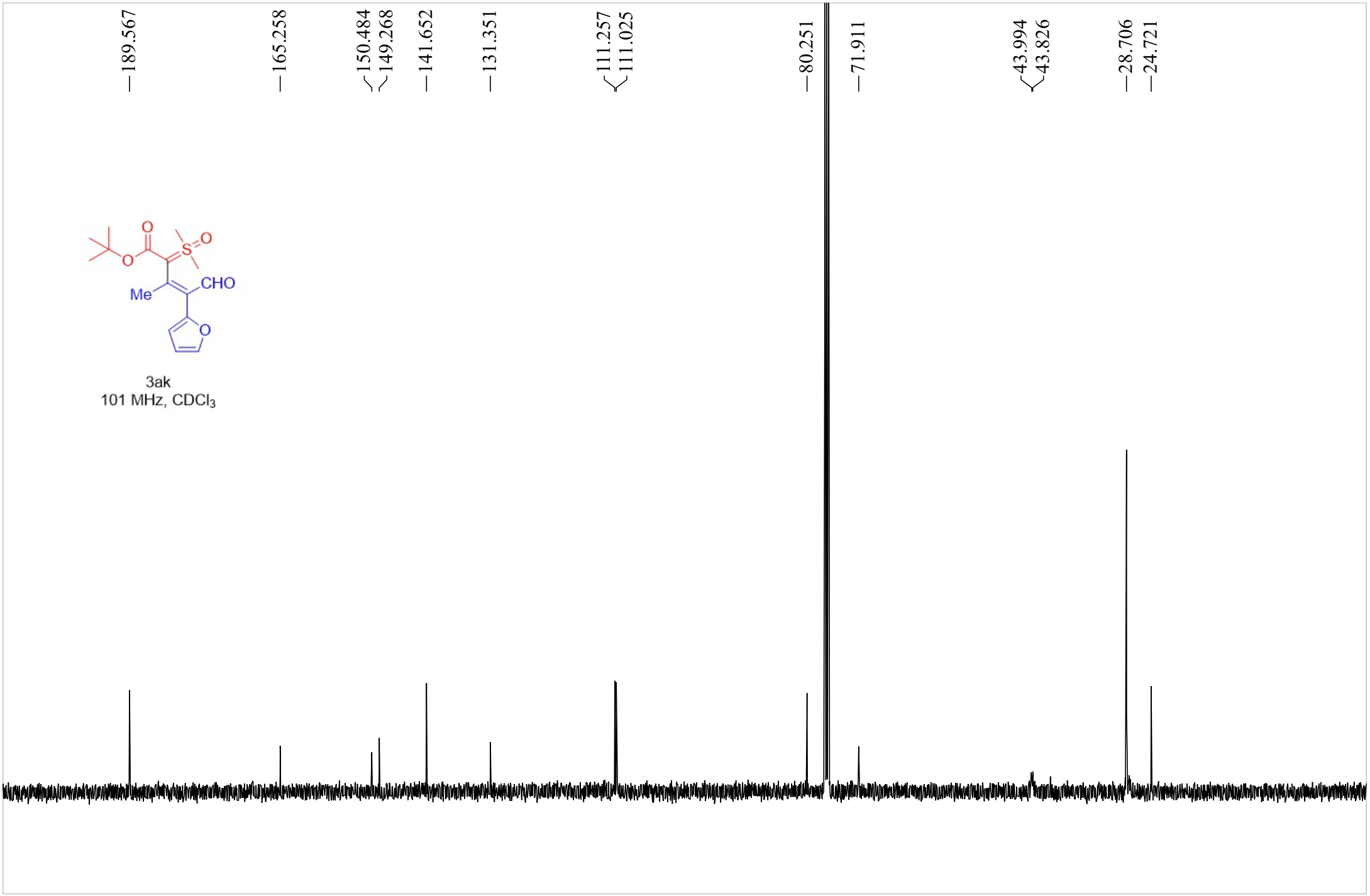
3ai
282 MHz, $CDCl_3$

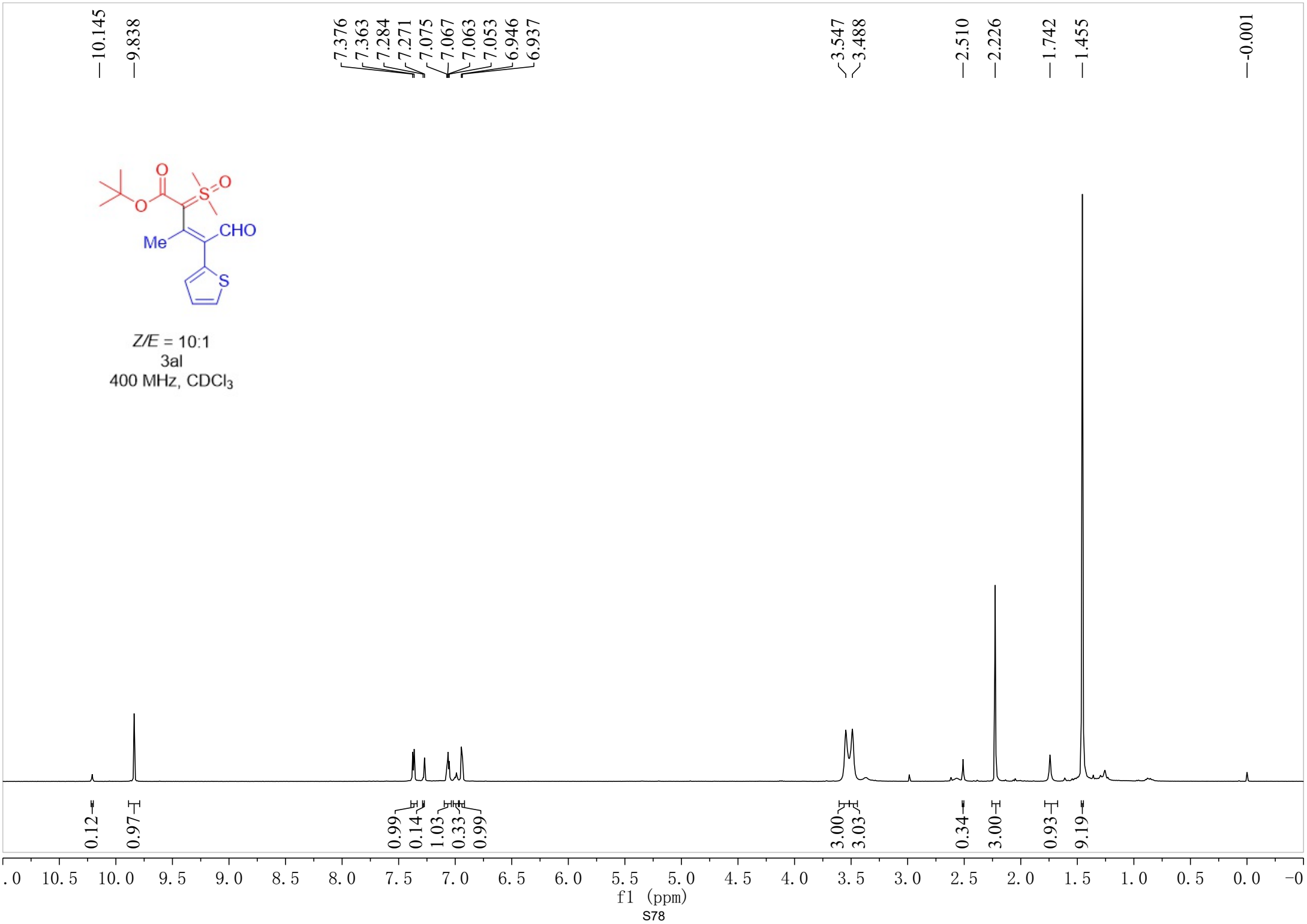


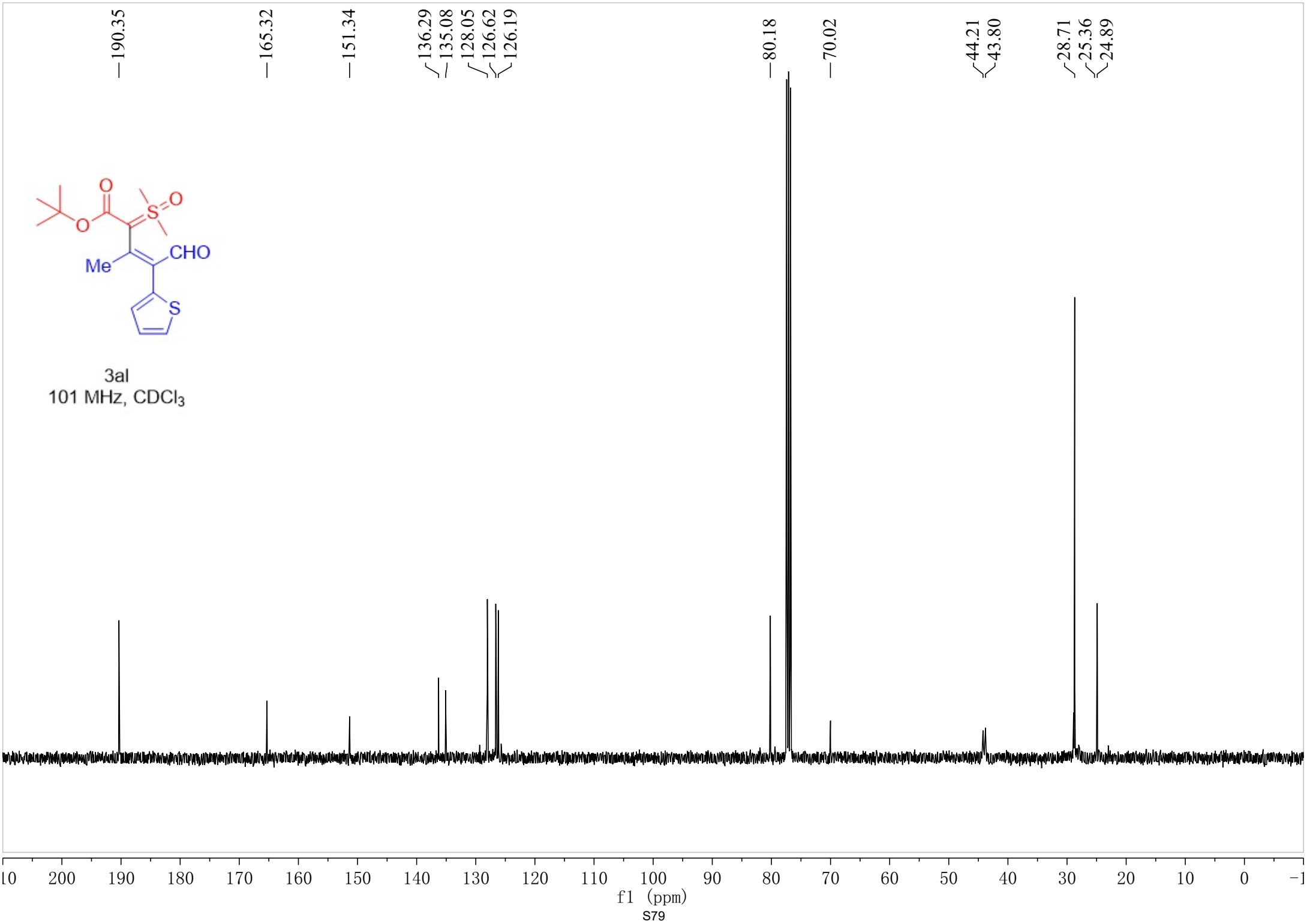

10.336
9.955
7.852
7.842
7.832
7.824
7.818
7.809
7.799
7.789
7.779
7.767
7.755
7.750
7.741
7.674
7.597
7.477
7.468
7.460
7.452
7.444
7.439
7.435
7.430
7.423
7.415
7.406
7.319
7.315
7.298
7.294
7.257
7.252
7.235
7.231
3.500
3.466
2.540
2.051
1.539
1.479
O
O
S=O
CHO
Me
Z/E = 7:1
3aj
400 MHz, CDCl3
0.14
0.97
3.02
0.56
0.15
1.00
2.05
0.27
0.18
1.08
3.01
2.95
0.43
3.04
1.31
9.02
f1 (ppm)

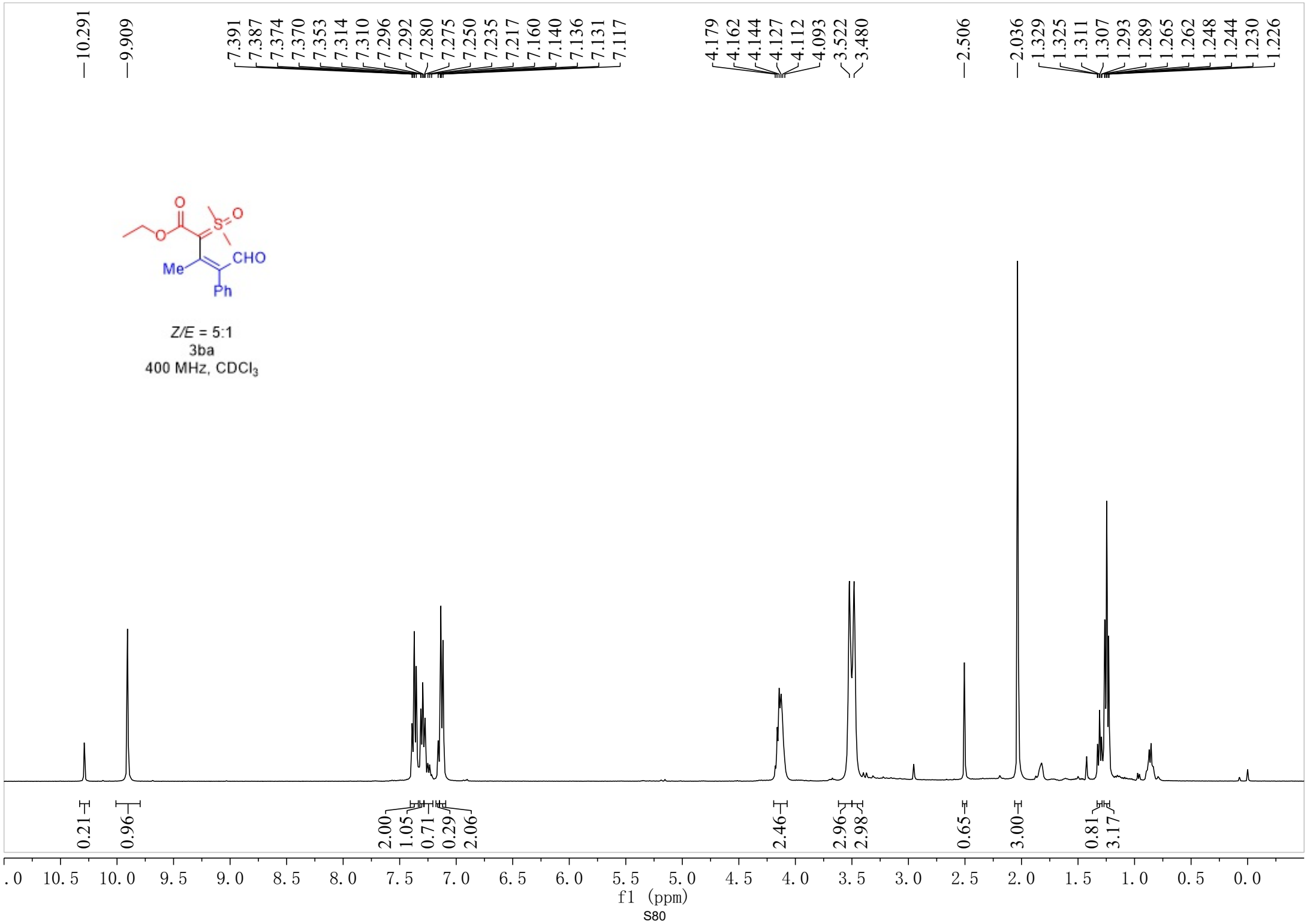

191.57
165.55
149.75
142.90
134.12
133.32
132.64
130.17
128.92
128.09
128.01
127.71
127.10
125.94
79.94
68.34
44.08
43.82
28.80
24.74
O
O
S
O
Me
CHO
3aj
101 MHz, CDCl3
f1 (ppm)

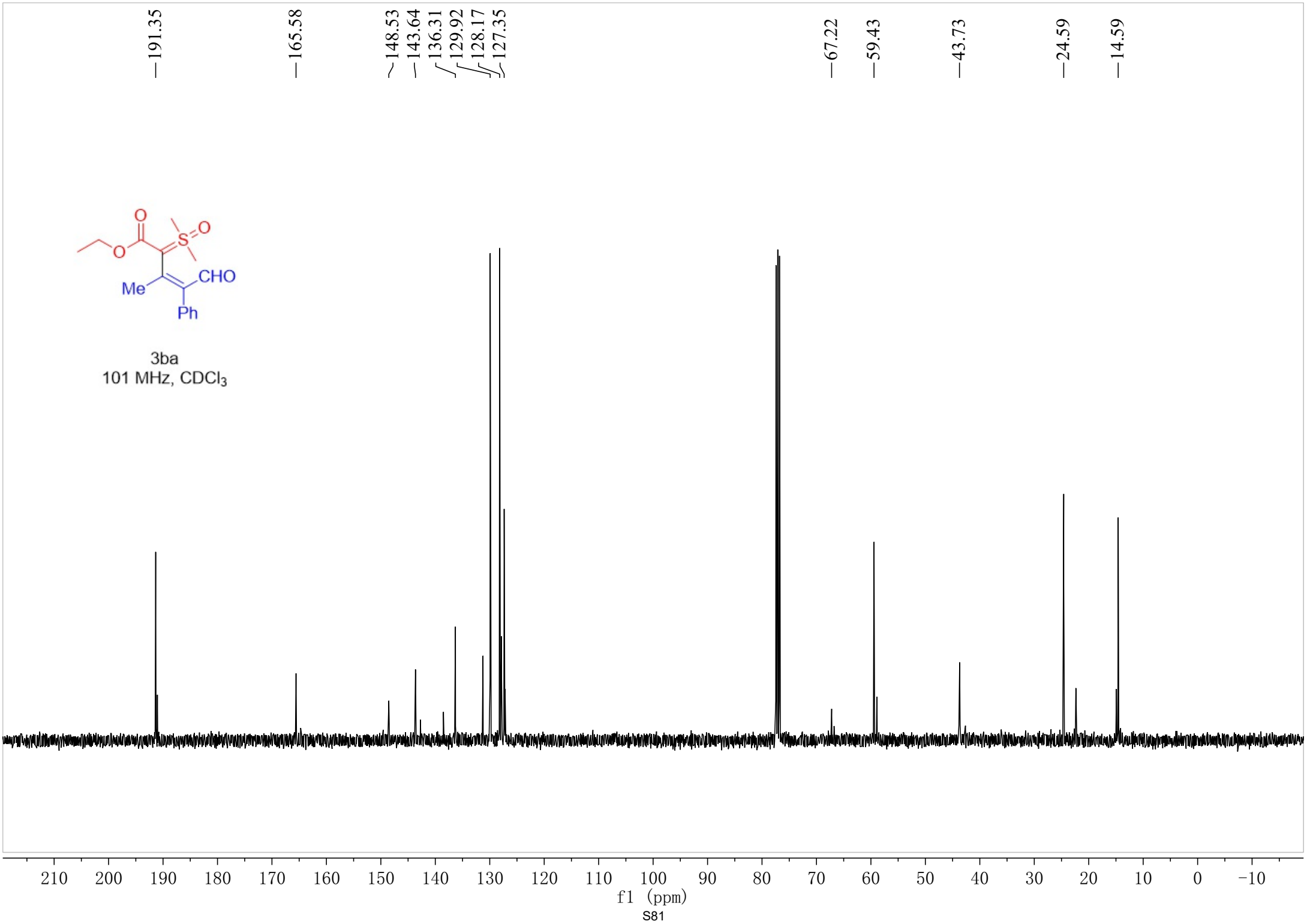

10.127
9.729
7.450
6.618
6.609
6.467
6.462
6.458
6.454
3.560
3.451
2.494
2.315
1.708
1.459
-0.117
O
O
S
O
Me
CHO
O
Z/E = 10:1
3ak
400 MHz, CDCl3
0.08
0.96
1.00
0.97
1.06
3.01
3.04
0.28
2.97
0.81
9.00
f1 (ppm)

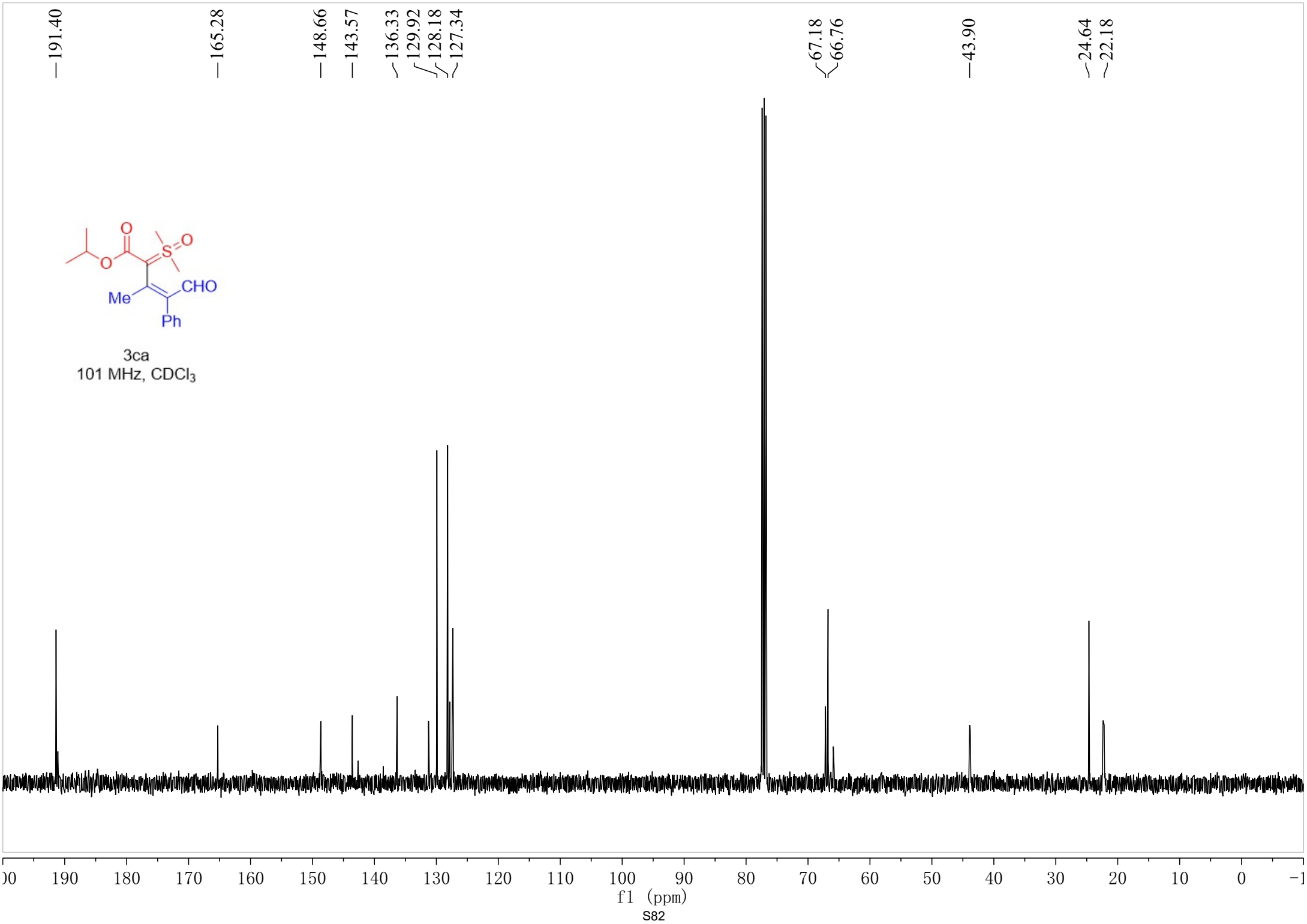

189.567
165.258
150.484
149.268
141.652
131.351
111.257
111.025
80.251
71.911
43.994
43.826
28.706
24.721
O
O
S
O
Me
CHO
O
3ak
101 MHz, CDCl3
f1 (ppm)

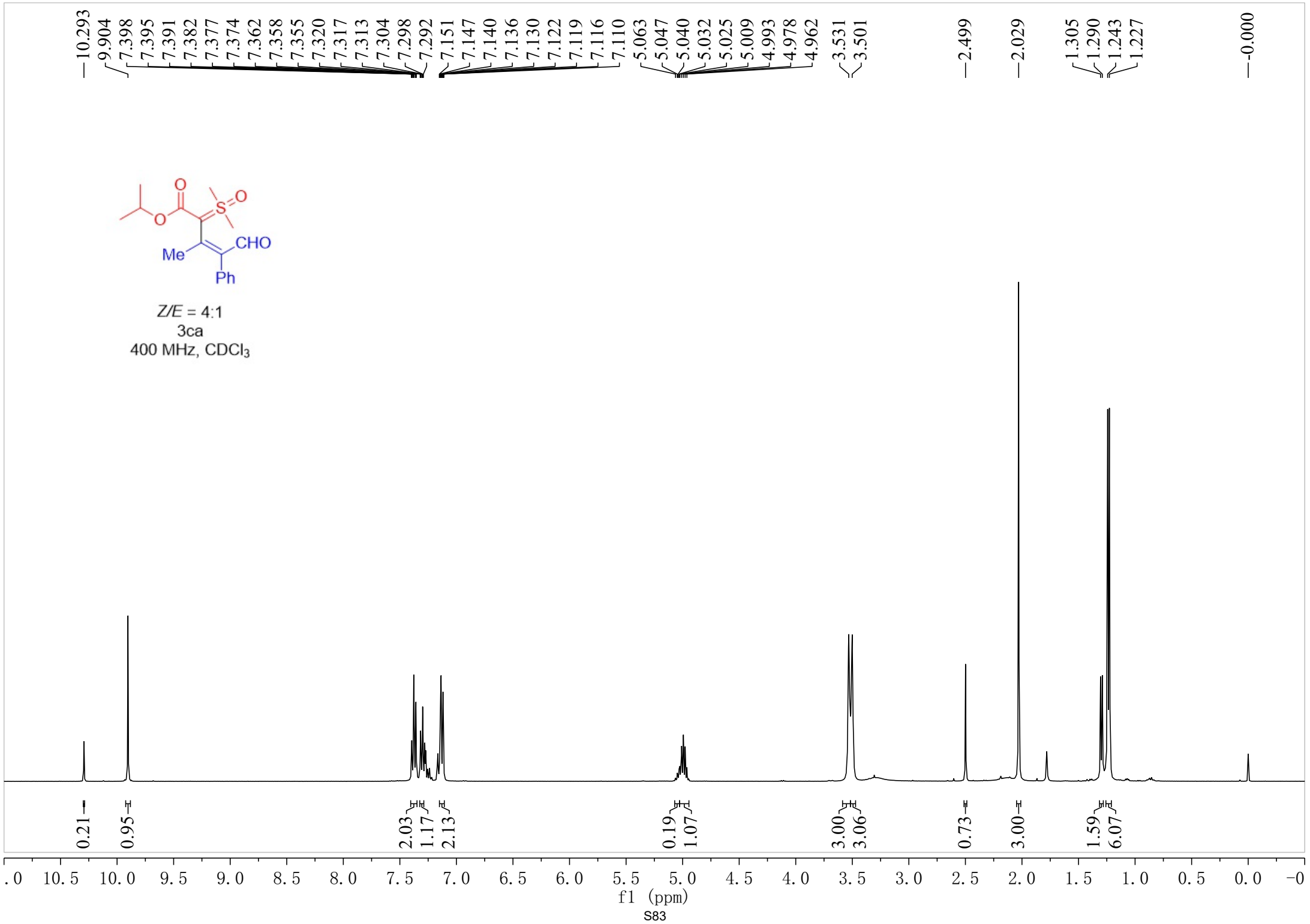

10.145
9.838
7.376
7.363
7.284
7.271
7.075
7.067
7.063
7.053
6.946
6.937
3.547
3.488
2.510
2.226
1.742
1.455
-0.001
O
O
S
O
CHO
Me
S
Z/E = 10:1
3al
400 MHz, CDCl3
0.12
0.97
0.99
0.14
1.03
0.33
0.99
3.00
3.03
0.34
3.00
0.93
9.19
f1 (ppm)

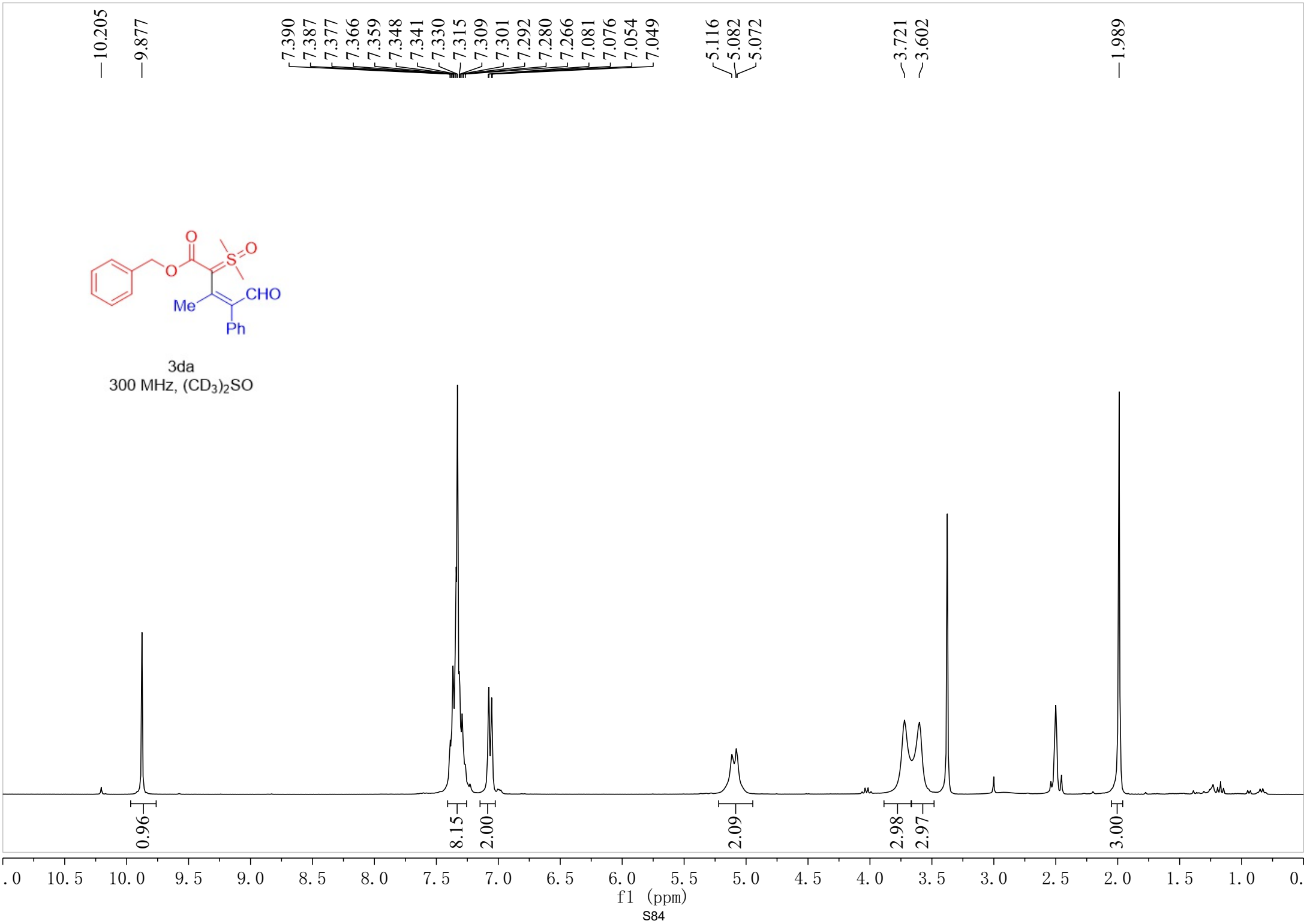

190.35
165.32
151.34
136.29
135.08
128.05
126.62
126.19
80.18
70.02
44.21
43.80
28.71
25.36
24.89
O
O
S
O
Me
CHO
S
3al
101 MHz, CDCl3
f1 (ppm)

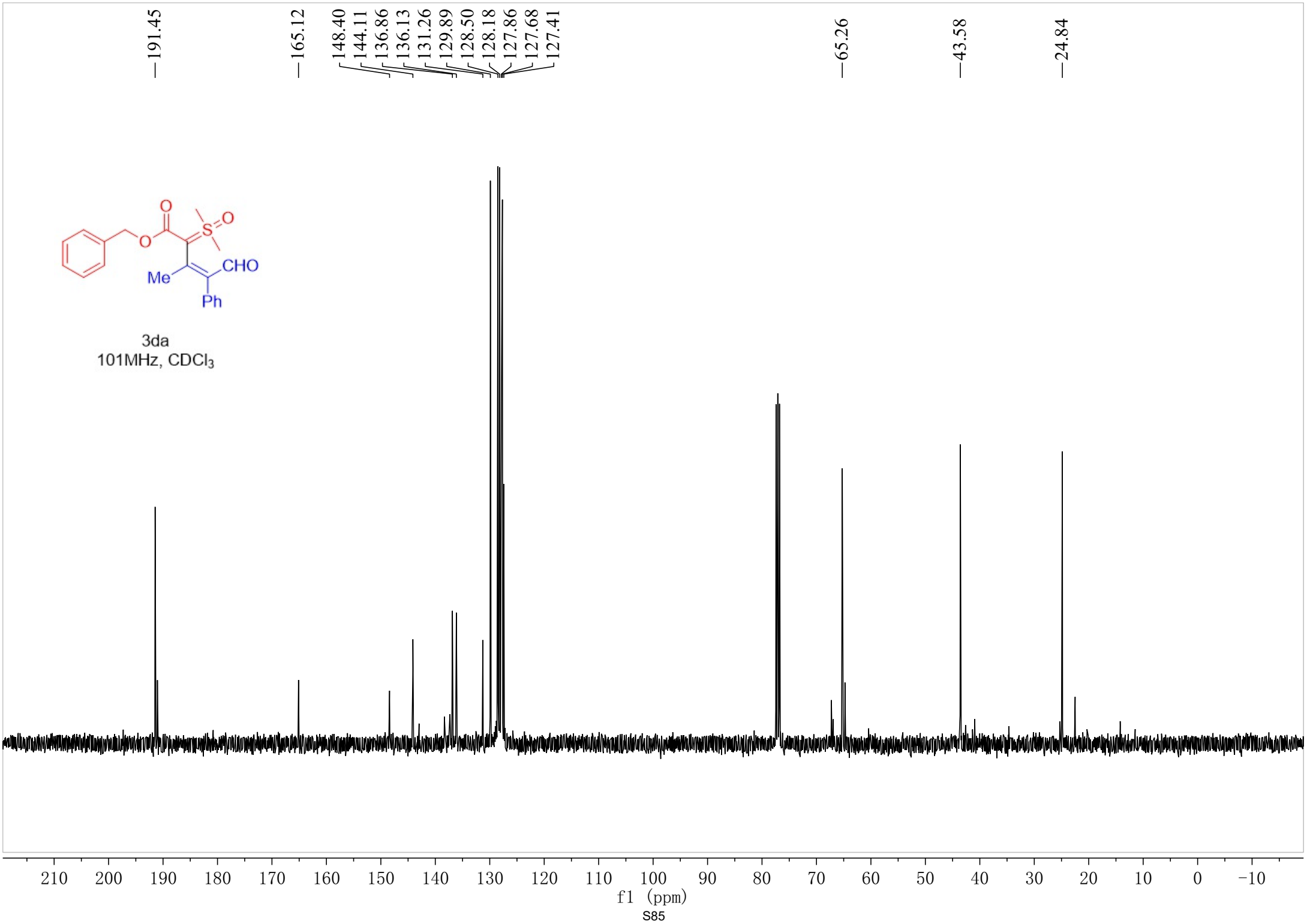

10.291
9.909
7.391
7.387
7.374
7.370
7.353
7.314
7.310
7.296
7.292
7.280
7.275
7.250
7.235
7.217
7.160
7.140
7.136
7.131
7.117
4.179
4.162
4.144
4.127
4.112
4.093
3.522
3.480
2.506
2.036
1.329
1.325
1.311
1.307
1.293
1.289
1.265
1.262
1.248
1.244
1.230
1.226
O
O
S
O
Me
CHO
Ph
Z/E = 5:1
3ba
400 MHz, CDCl3
0.21
0.96
2.00
1.05
0.71
0.29
2.06
2.46
2.96
2.98
0.65
3.00
0.81
3.17
f1 (ppm)

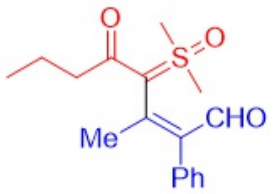

191.35
165.58
148.53
143.64
136.31
129.92
128.17
127.35
67.22
59.43
43.73
24.59
14.59
O
O
S
O
Me
CHO
Ph
3ba
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


191.40
165.28
148.66
143.57
136.33
129.92
128.18
127.34
67.18
66.76
43.90
24.64
22.18
O
O
S
O
Me
CHO
Ph
3ca
101 MHz, CDCl3
f1 (ppm)

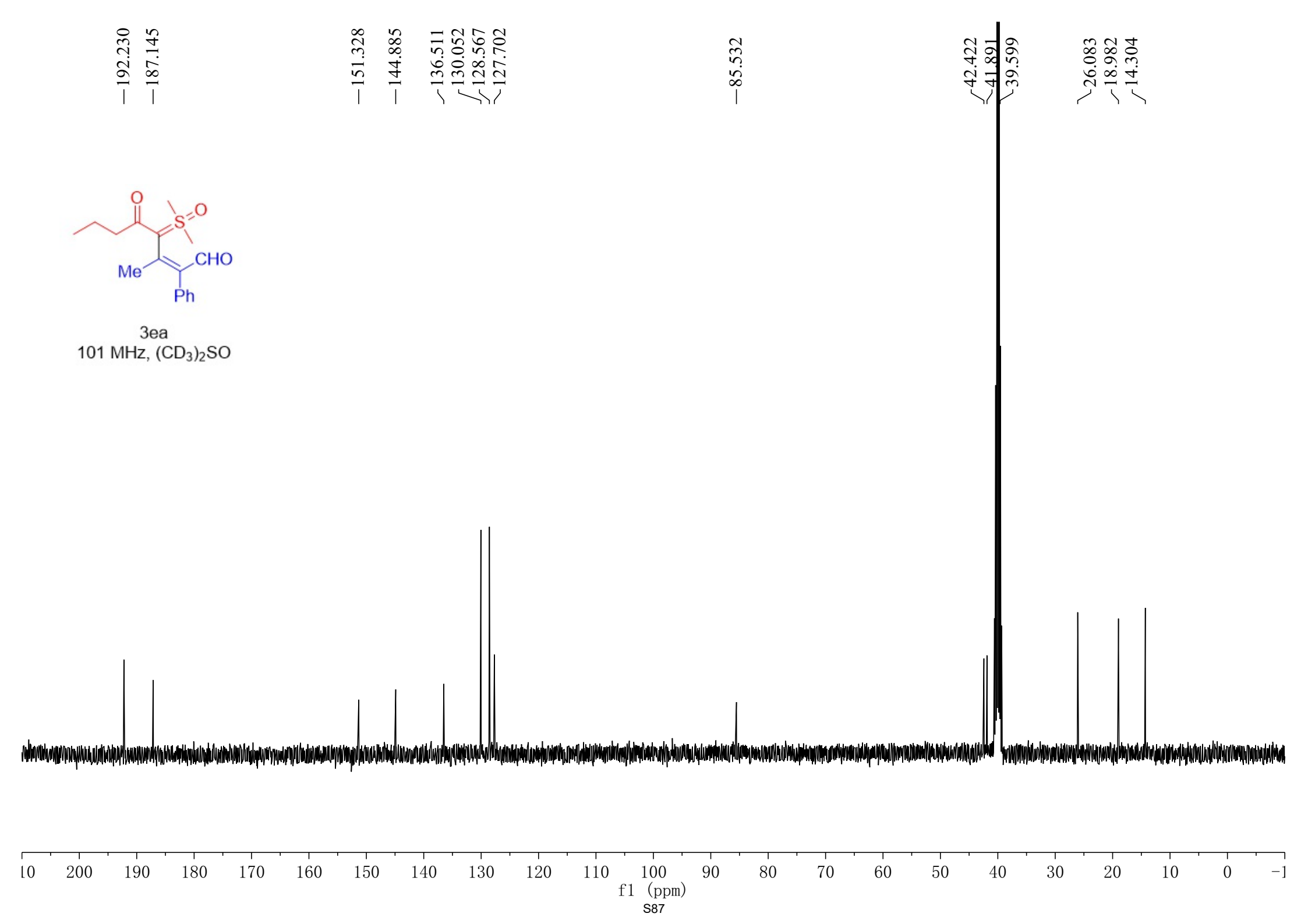

10.293
9.904
7.398
7.395
7.391
7.382
7.377
7.374
7.362
7.358
7.355
7.320
7.317
7.313
7.304
7.298
7.292
7.151
7.147
7.140
7.136
7.130
7.122
7.119
7.116
7.110
5.063
5.047
5.040
5.032
5.025
5.009
4.993
4.978
4.962
3.531
3.501
2.499
2.029
1.305
1.290
1.243
1.227
-0.000
O
O
S
O
CHO
Me
Ph
Z/E = 4:1
3ca
400 MHz, CDCl3
0.21
0.95
2.03
1.17
2.13
0.19
1.07
3.00
3.06
0.73
3.00
1.59
6.07
f1 (ppm)

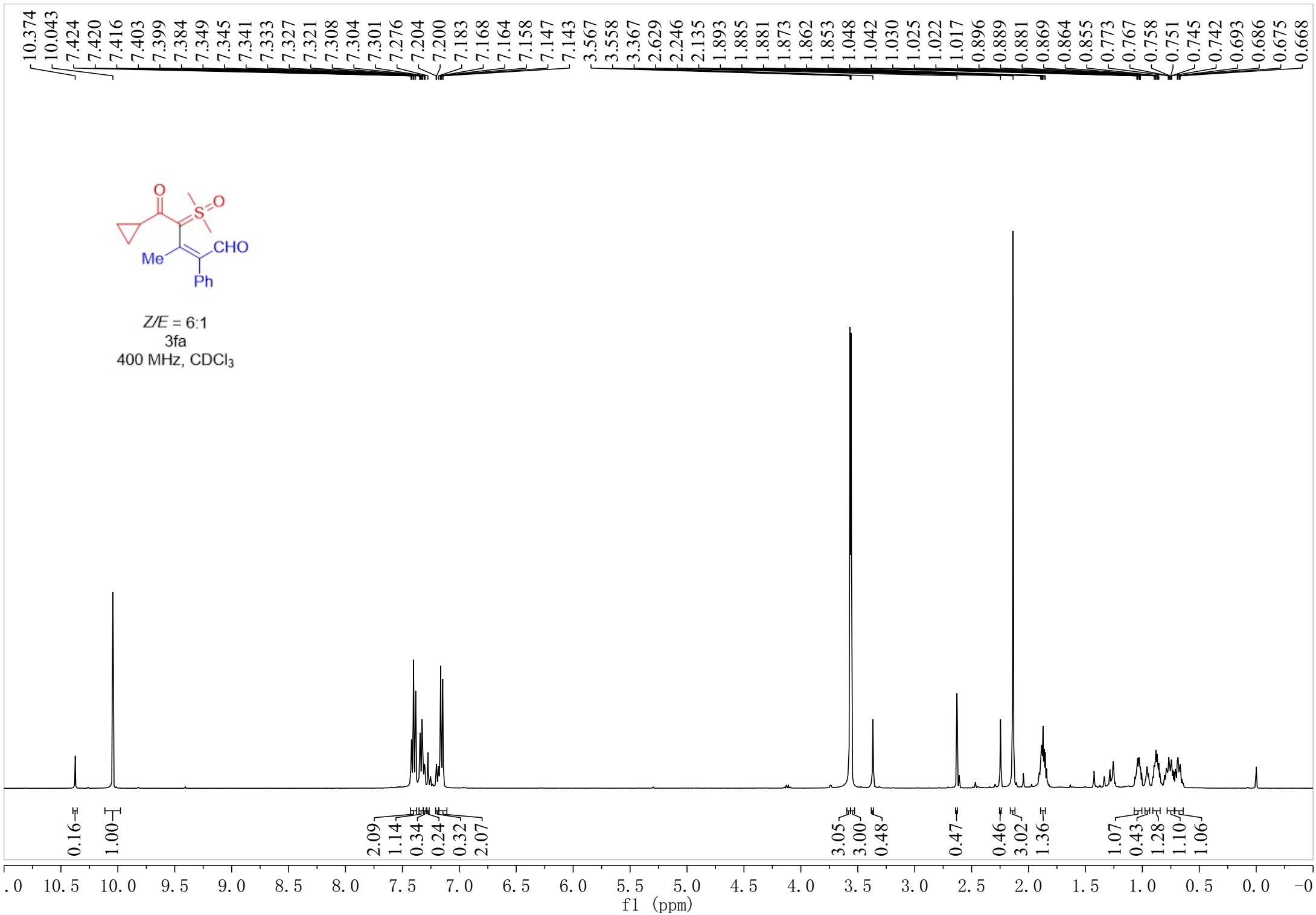

10.205
9.877
7.390
7.387
7.377
7.366
7.359
7.348
7.341
7.330
7.315
7.309
7.301
7.292
7.280
7.266
7.081
7.076
7.054
7.049
5.116
5.082
5.072
3.721
3.602
1.989
O
O
S
O
Me
CHO
Ph
3da
300 MHz, (CD3)2SO
0.96
8.15
2.00
2.09
2.98
2.97
3.00
f1 (ppm)

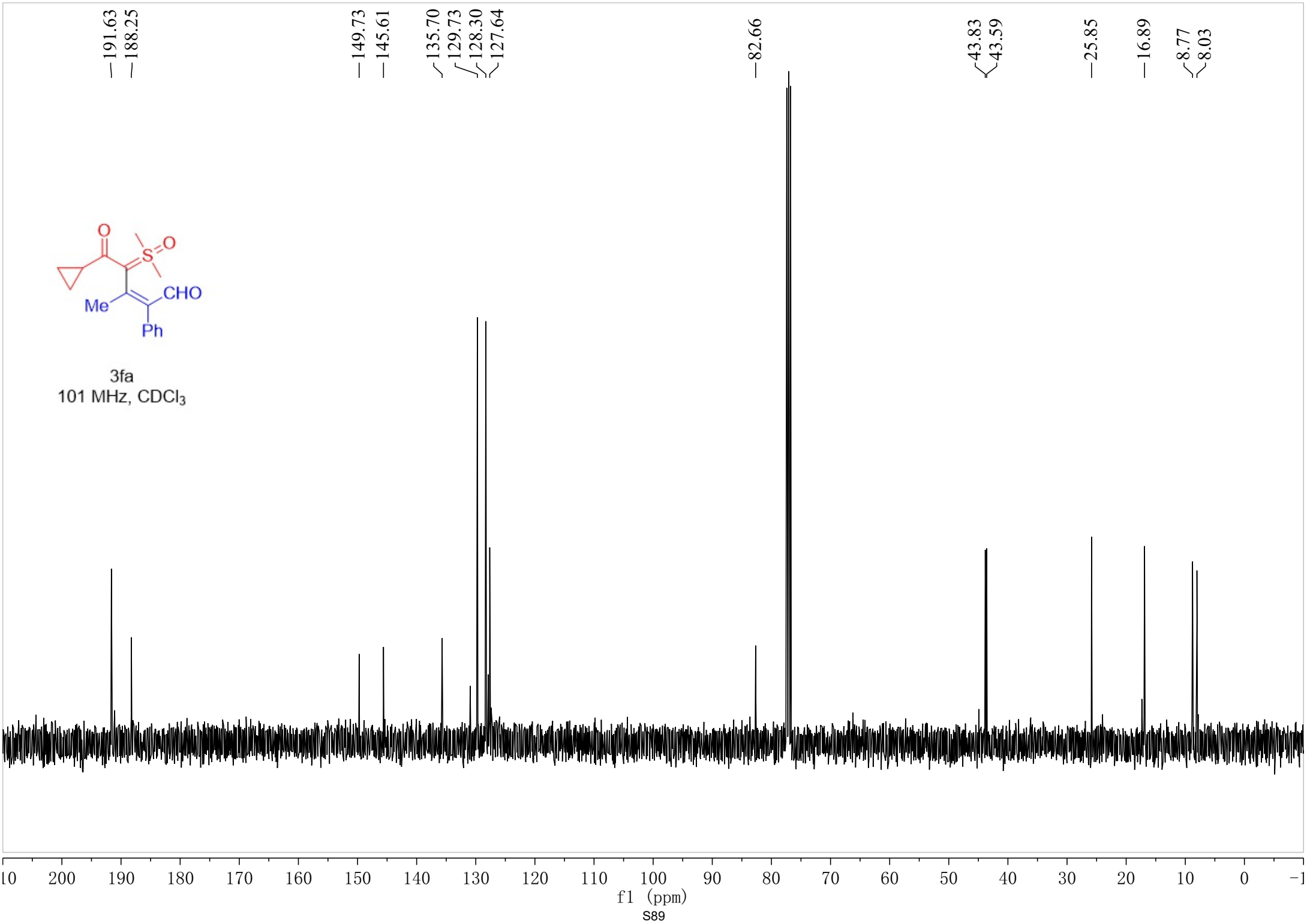

191.45
165.12
148.40
144.11
136.86
136.13
131.26
129.89
128.50
128.18
127.86
127.68
127.41
65.26
43.58
24.84
O
O
S
O
Me
CHO
Ph
3da
101MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

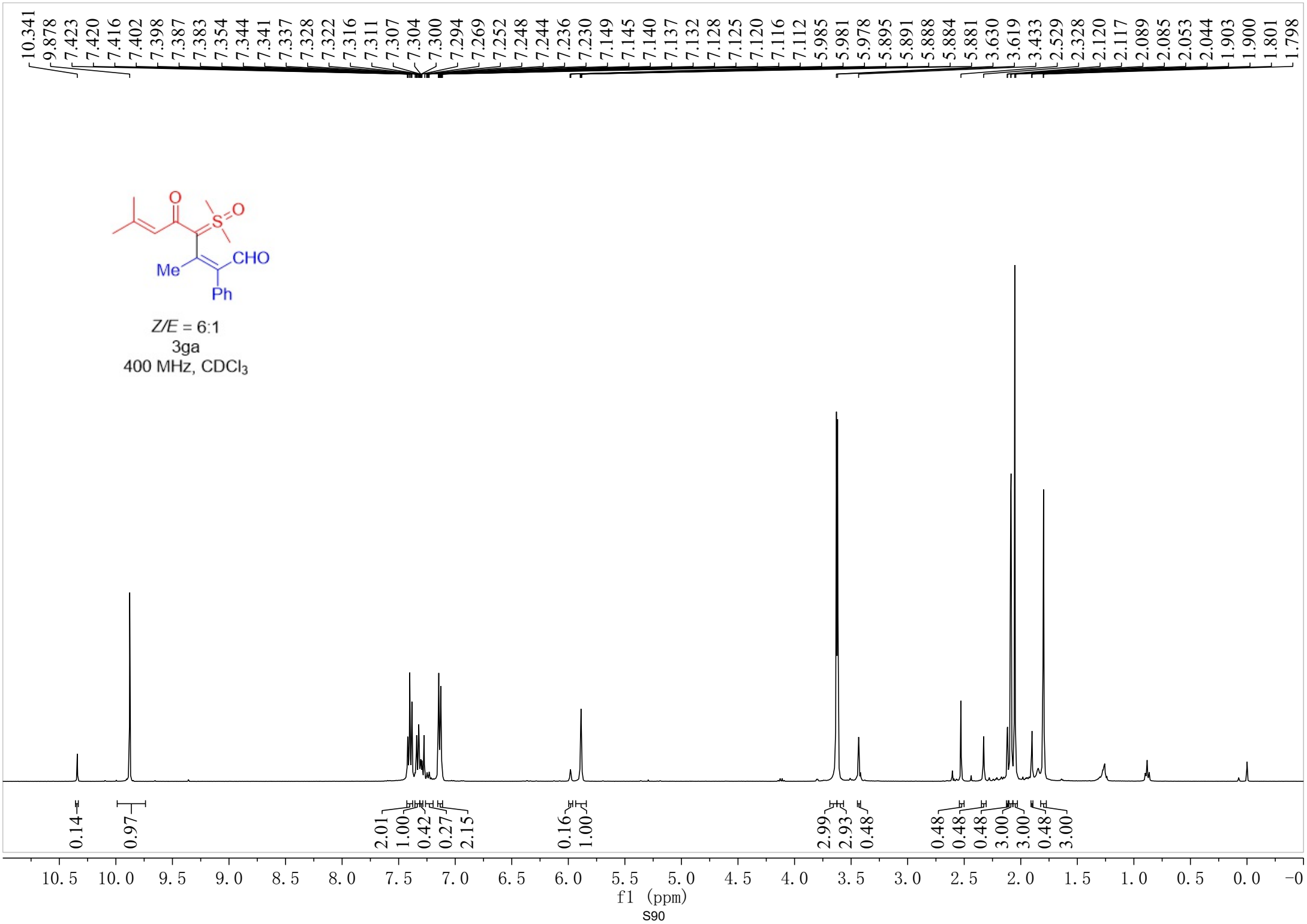


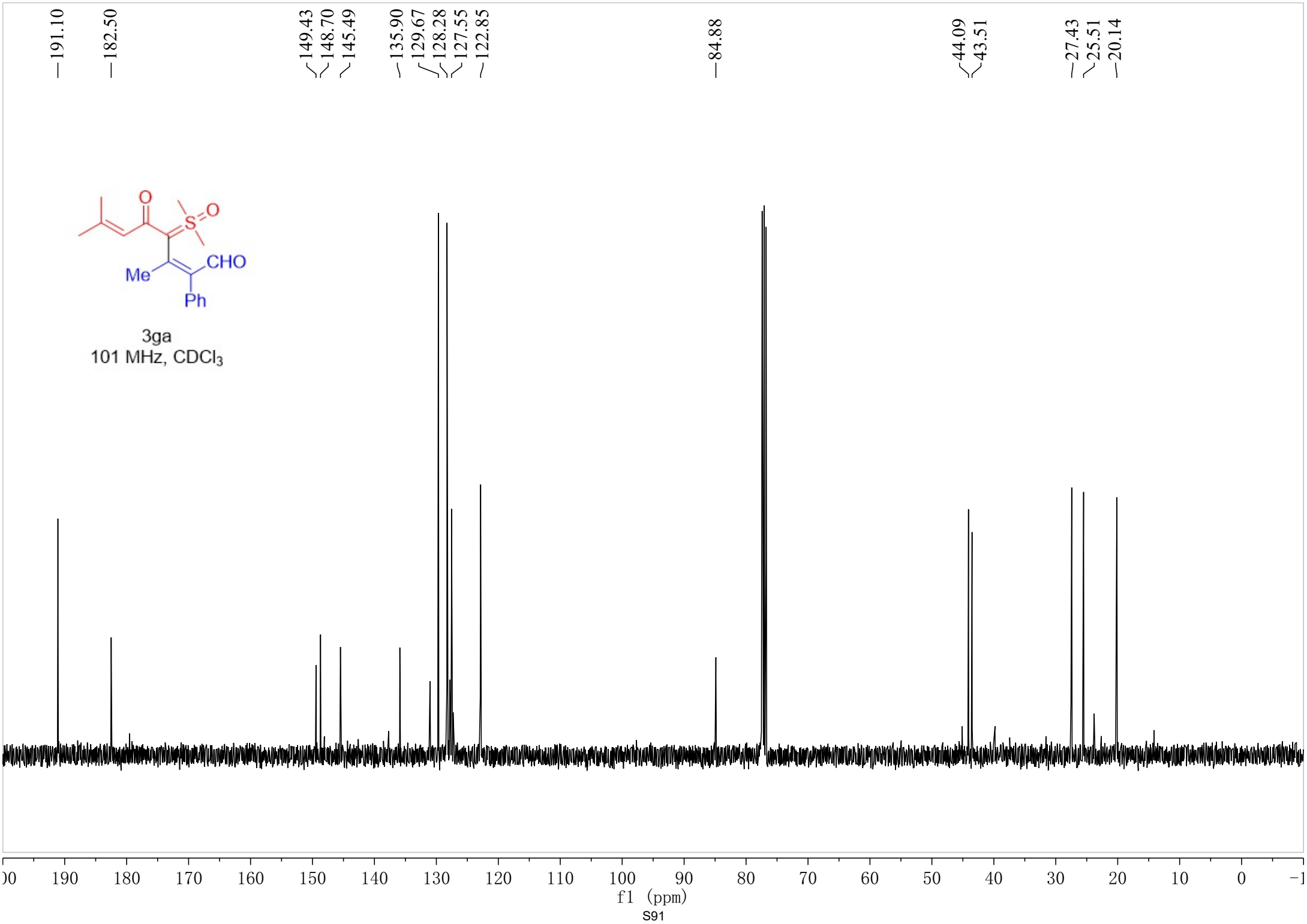
3ea
400 MHz, $(CD_3)_2SO$

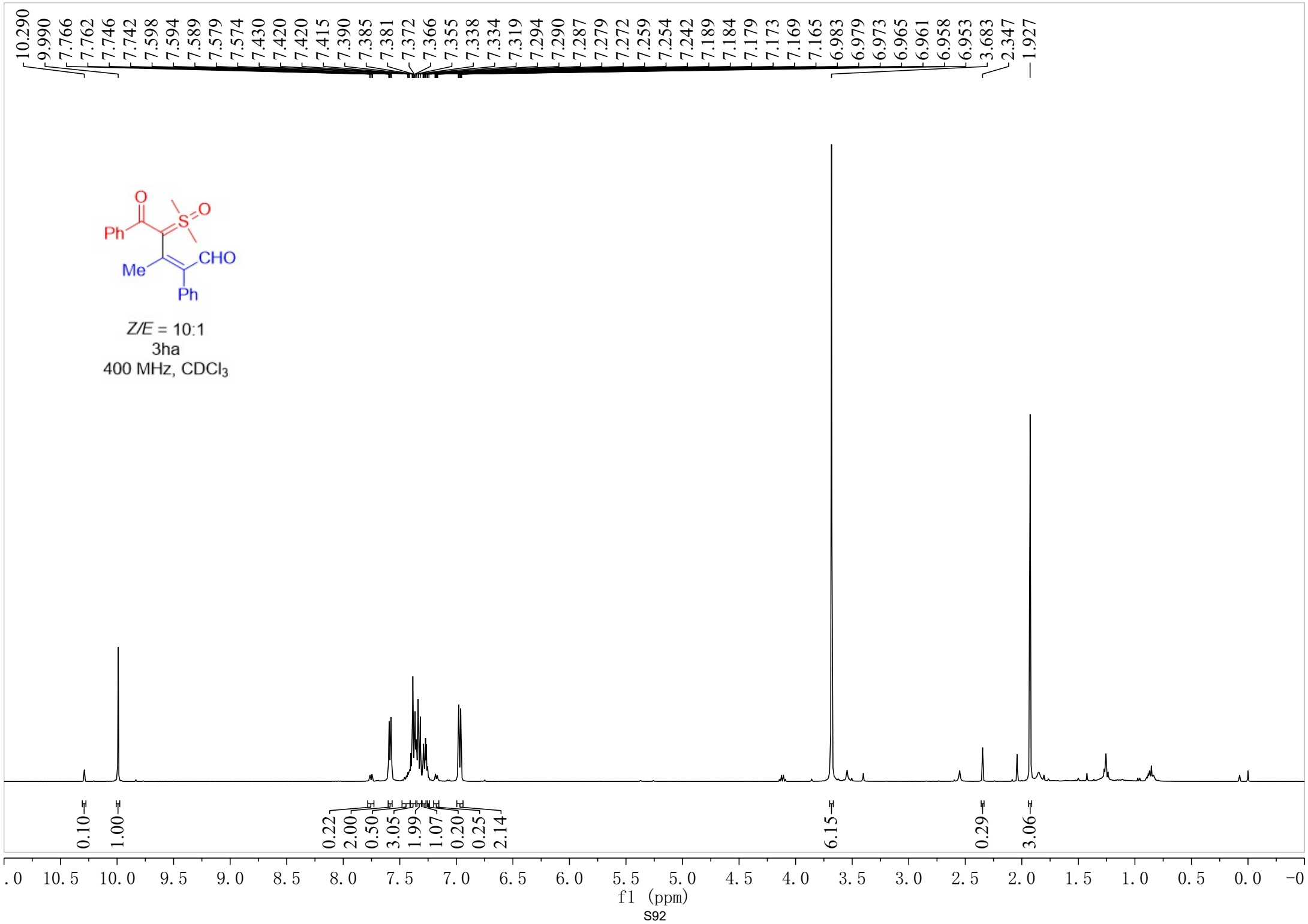

192.230
187.145
151.328
144.885
136.511
130.052
128.567
127.702
85.532
42.422
41.891
39.599
26.083
18.982
14.304
O
S
O
CHO
Me
Ph
3ea
101 MHz, (CD3)2SO
f1 (ppm)

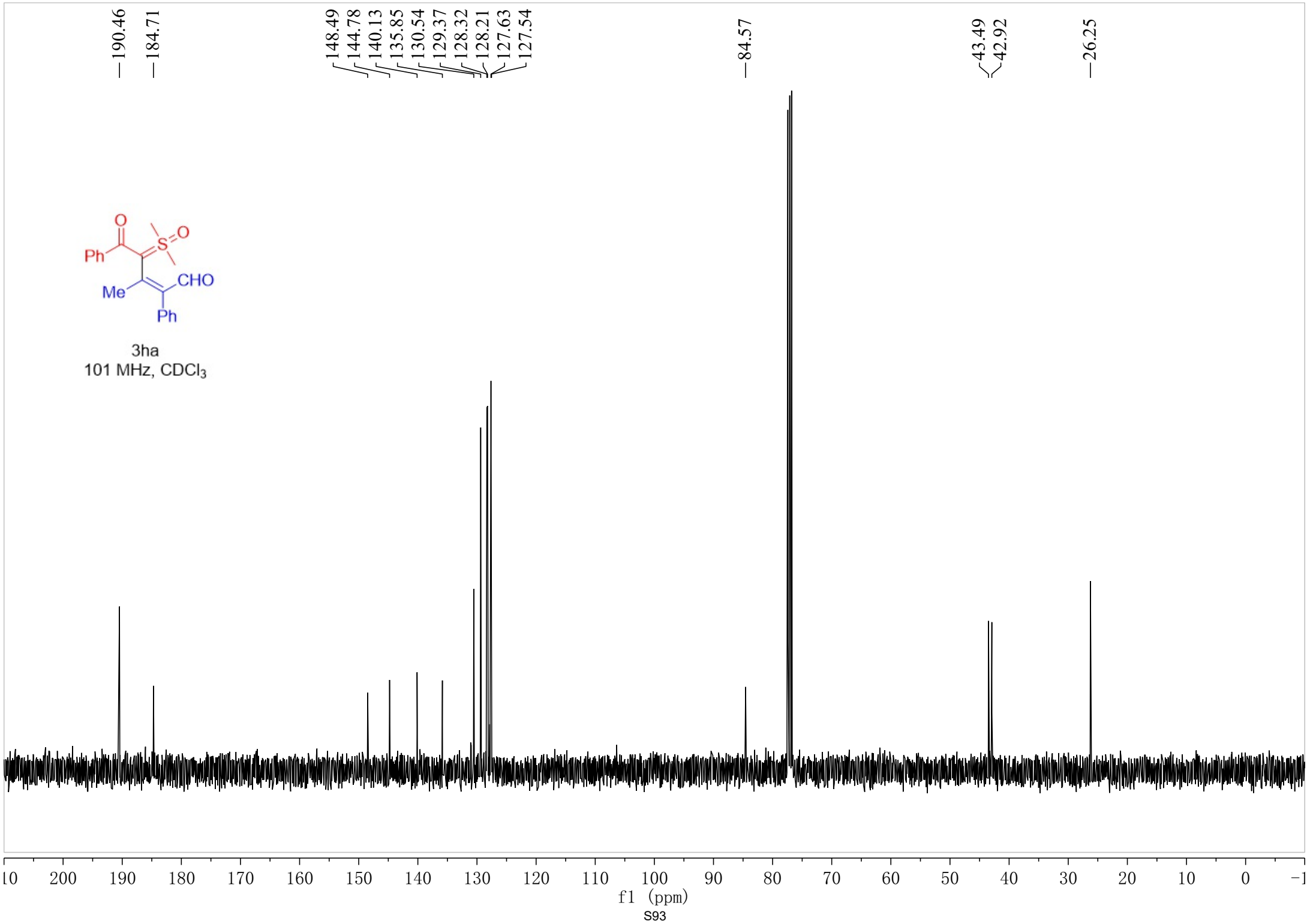

10.374
10.043
7.424
7.420
7.416
7.403
7.399
7.384
7.349
7.345
7.341
7.333
7.327
7.321
7.308
7.304
7.301
7.276
7.204
7.200
7.183
7.168
7.164
7.158
7.147
7.143
3.567
3.558
3.367
2.629
2.246
2.135
1.893
1.885
1.881
1.873
1.862
1.853
1.048
1.042
1.030
1.025
1.022
1.017
0.896
0.889
0.881
0.869
0.864
0.855
0.773
0.767
0.758
0.751
0.745
0.742
0.693
0.686
0.675
0.668
O
S
O
CHO
Me
Ph
Z/E = 6:1
3fa
400 MHz, CDCl3
0.16
1.00
2.09
1.14
0.34
0.24
0.32
2.07
3.05
3.00
0.48
0.47
0.46
3.02
1.36
1.07
0.43
1.28
1.10
1.06
f1 (ppm)

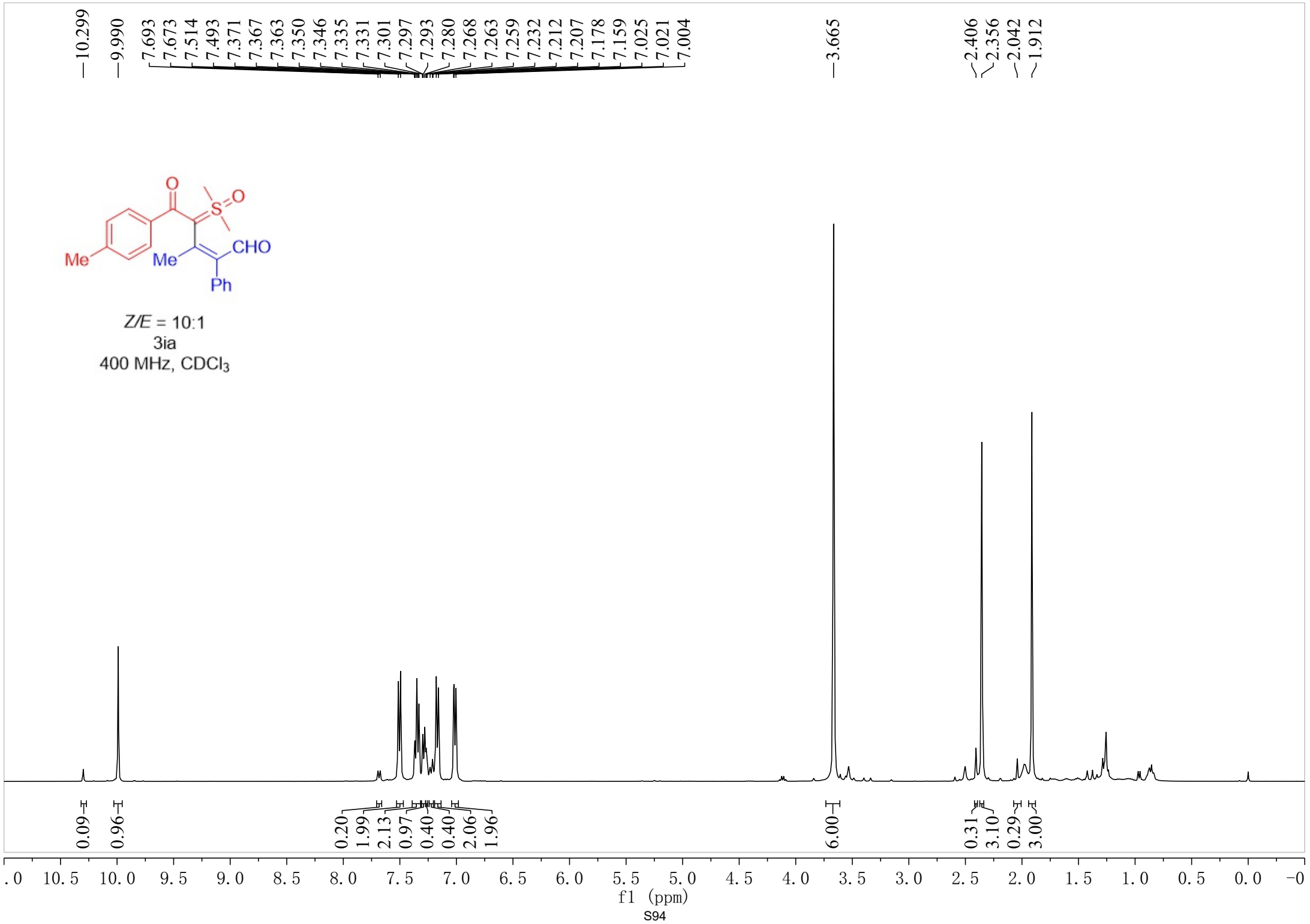

191.63
188.25
149.73
145.61
135.70
129.73
128.30
127.64
82.66
43.83
43.59
25.85
16.89
8.77
8.03
O
S
O
CHO
Me
Ph
3fa
101 MHz, CDCl3
f1 (ppm)

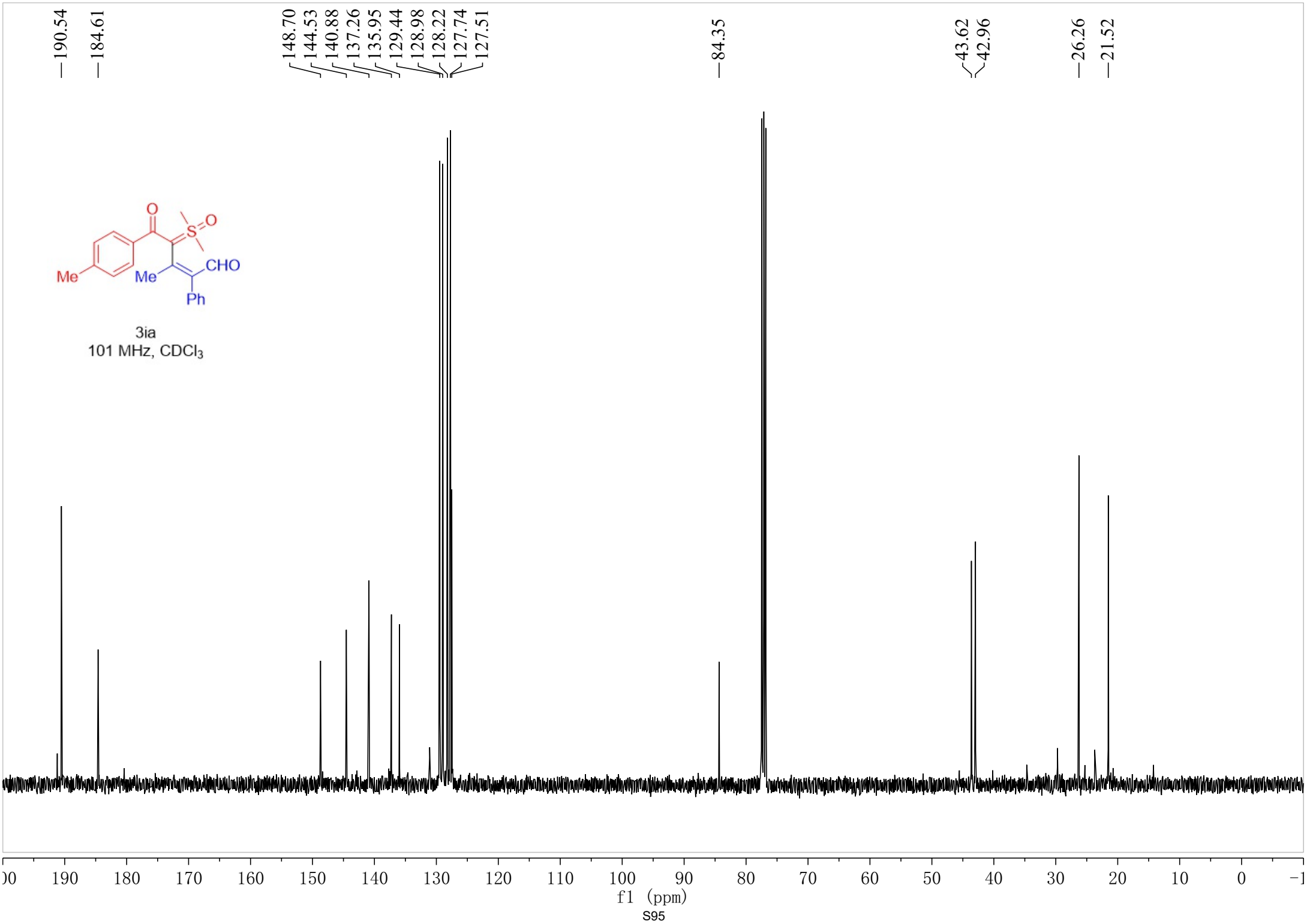

10.341
9.878
7.423
7.420
7.416
7.402
7.398
7.387
7.383
7.354
7.344
7.341
7.337
7.328
7.322
7.316
7.311
7.307
7.304
7.300
7.294
7.269
7.252
7.248
7.244
7.236
7.230
7.149
7.145
7.140
7.137
7.132
7.128
7.125
7.120
7.116
7.112
5.985
5.981
5.978
5.895
5.891
5.888
5.884
5.881
3.630
3.619
3.433
2.529
2.328
2.120
2.117
2.089
2.085
2.053
2.044
1.903
1.900
1.801
1.798
O
S
O
CHO
Me
Ph
Z/E = 6:1
3ga
400 MHz, CDCl3
0.14
0.97
2.01
1.00
0.42
0.27
2.15
0.16
1.00
2.99
2.93
0.48
0.48
0.48
0.48
3.00
3.00
0.48
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)

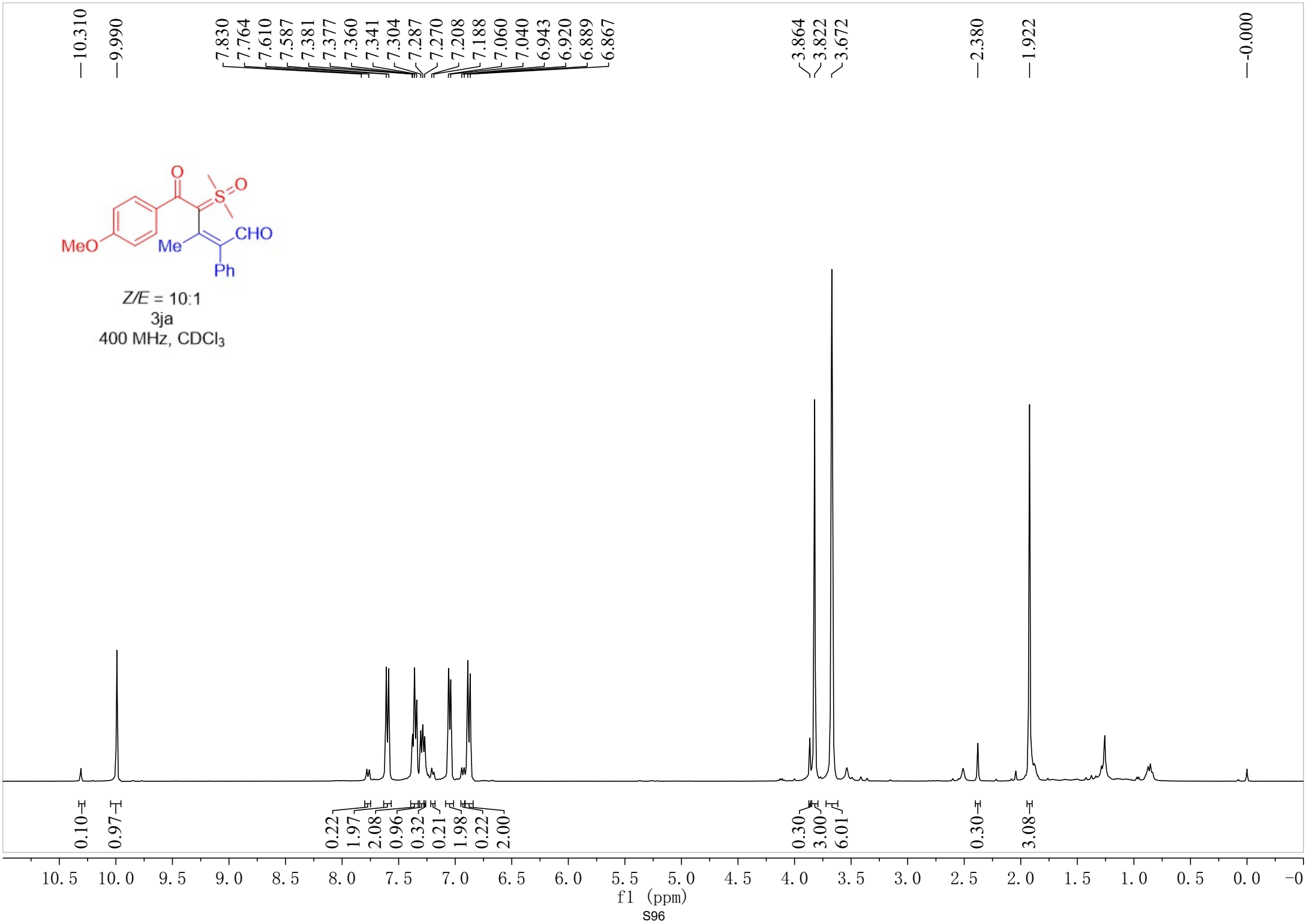

191.10
182.50
149.43
148.70
145.49
135.90
129.67
128.28
127.55
122.85
84.88
44.09
43.51
27.43
25.51
20.14
O
S
O
CHO
Me
Ph
3ga
101 MHz, CDCl3
f1 (ppm)

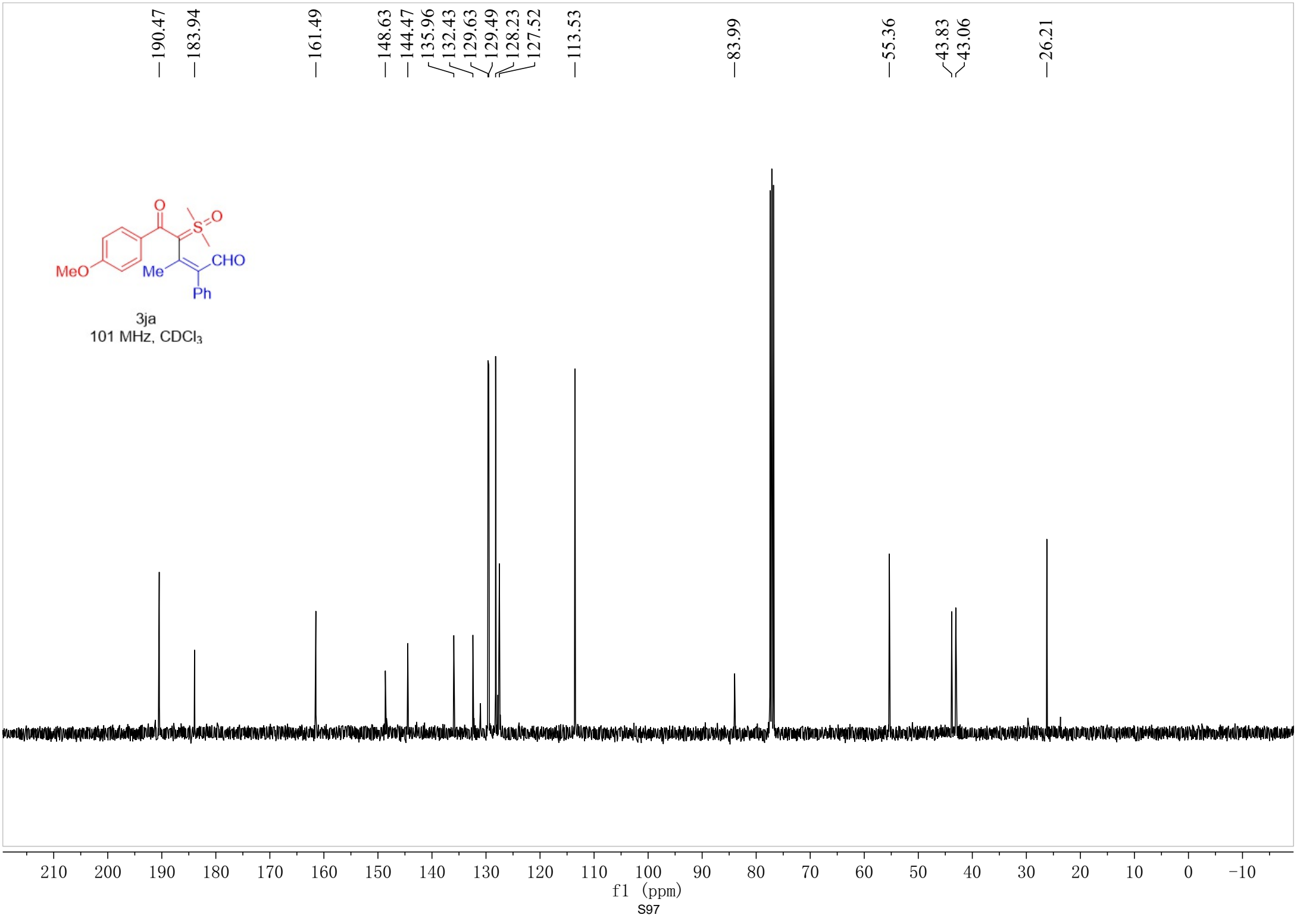

10.290
9.990
7.766
7.762
7.746
7.742
7.598
7.594
7.589
7.579
7.574
7.430
7.420
7.420
7.415
7.390
7.385
7.381
7.372
7.366
7.355
7.338
7.334
7.319
7.294
7.290
7.287
7.279
7.272
7.259
7.254
7.242
7.189
7.184
7.179
7.173
7.169
7.165
6.983
6.979
6.973
6.965
6.961
6.958
6.953
3.683
2.347
1.927
Ph
O
S
O
CHO
Me
Ph
Z/E = 10:1
3ha
400 MHz, CDCl3
0.10
1.00
0.22
2.00
0.50
3.05
1.99
1.07
0.20
0.25
2.14
6.15
0.29
3.06
f1 (ppm)

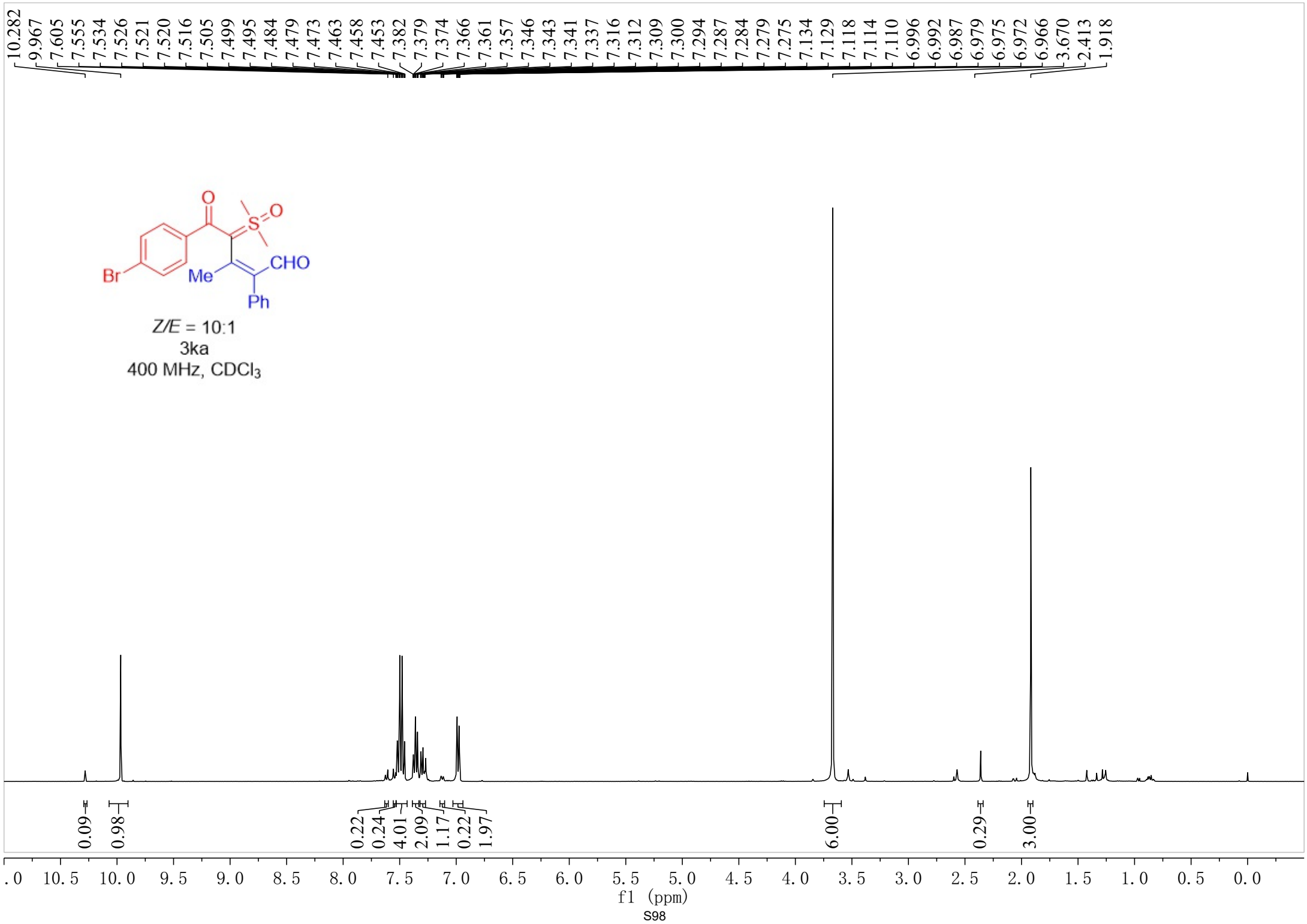

190.46
184.71
148.49
144.78
140.13
135.85
130.54
129.37
128.32
128.21
127.63
127.54
84.57
43.49
42.92
26.25
Ph
O
S
O
Me
CHO
Ph
3ha
101 MHz, CDCl3
f1 (ppm)

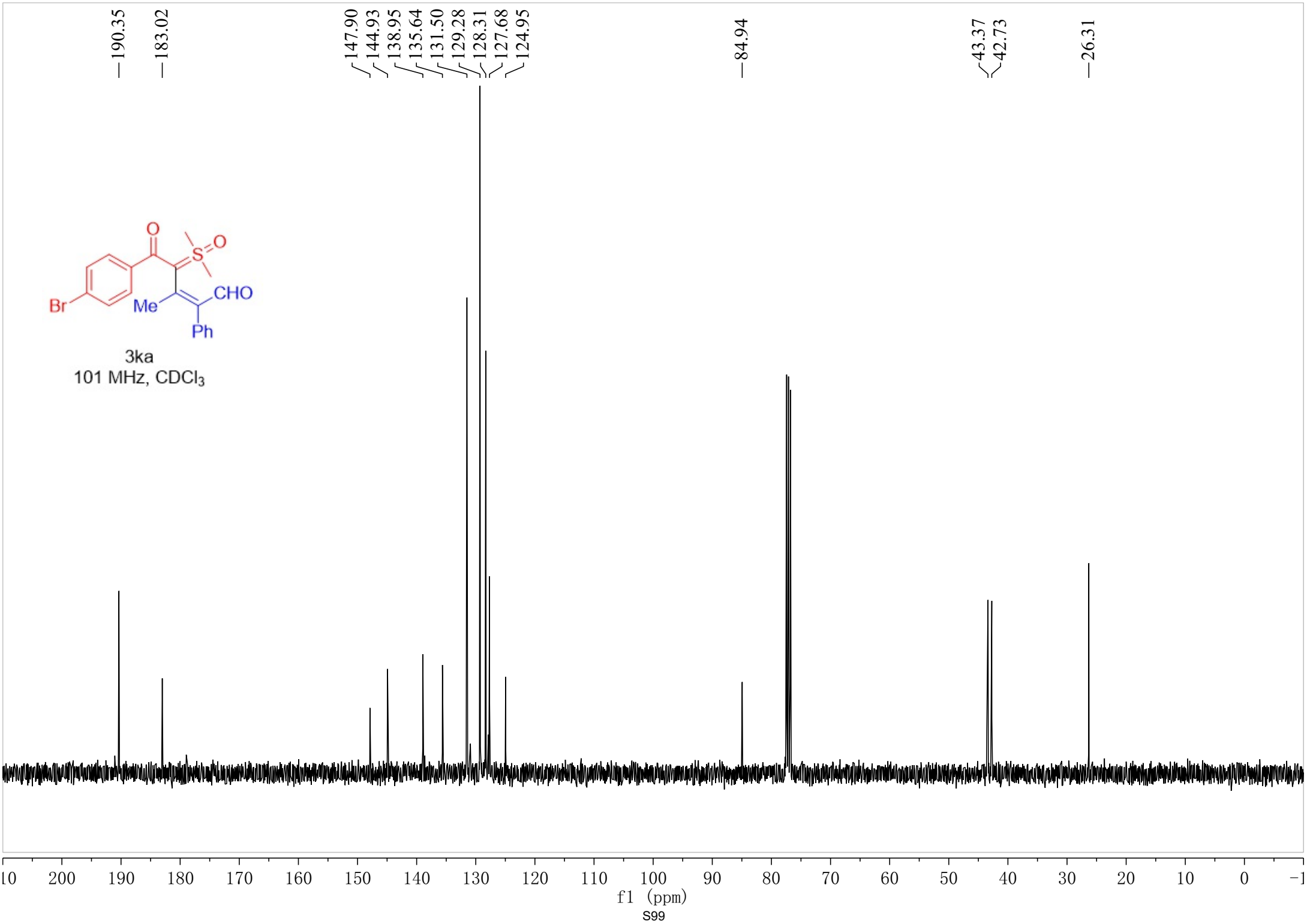

10.299
9.990
7.693
7.673
7.514
7.493
7.371
7.367
7.363
7.350
7.346
7.335
7.331
7.301
7.297
7.293
7.280
7.268
7.263
7.259
7.232
7.212
7.207
7.178
7.159
7.025
7.021
7.004
3.665
2.406
2.356
2.042
1.912
O
S
O
Me
Me
CHO
Ph
Z/E = 10:1
3ia
400 MHz, CDCl3
0.09
0.96
0.20
1.99
2.13
0.97
0.40
0.40
2.06
1.96
6.00
0.31
3.10
0.29
3.00
f1 (ppm)

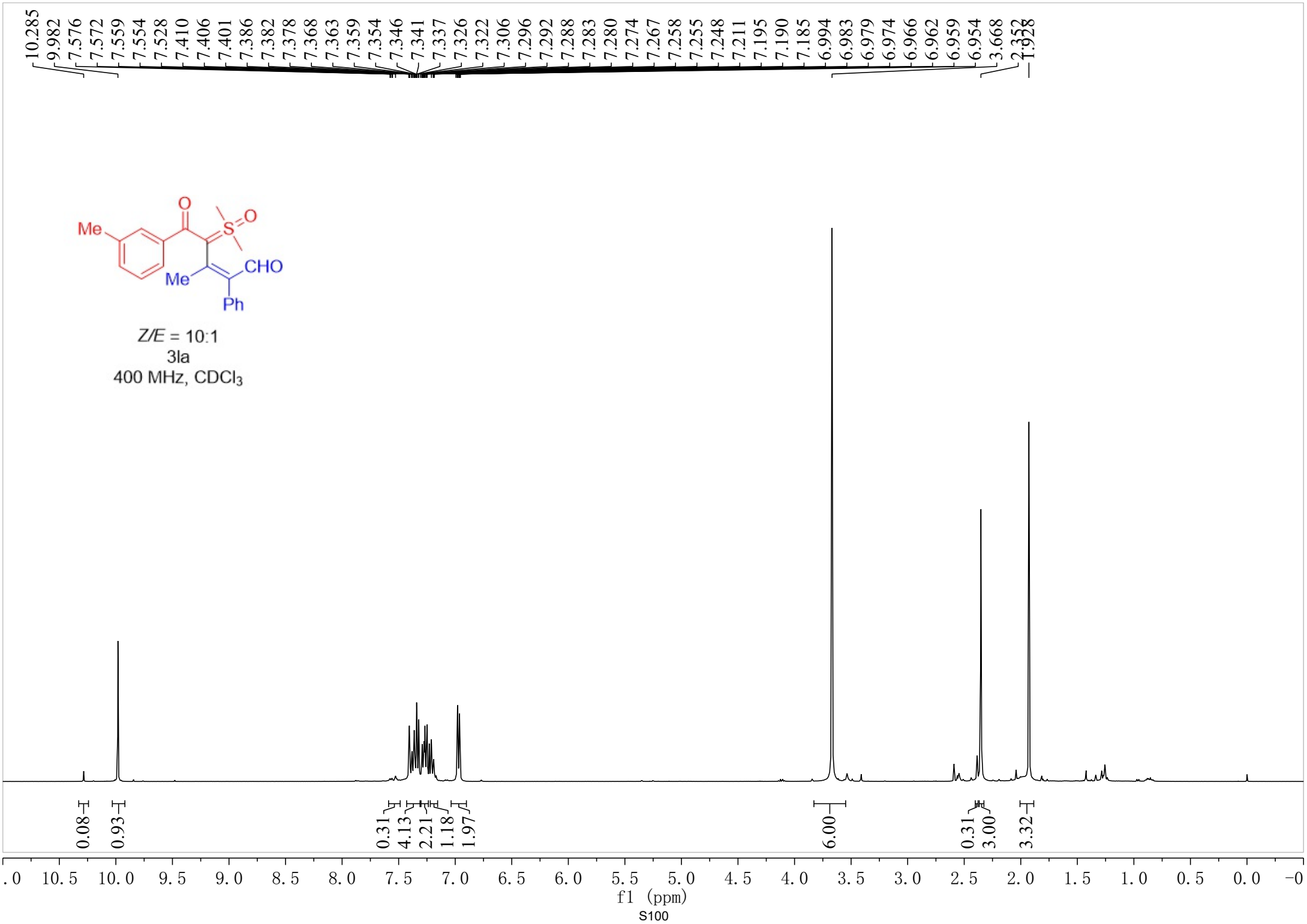

190.54
184.61
148.70
144.53
140.88
137.26
135.95
129.44
128.98
128.22
127.74
127.51
84.35
43.62
42.96
26.26
21.52
O
S
O
Me
Me
CHO
Ph
3ia
101 MHz, CDCl3
f1 (ppm)

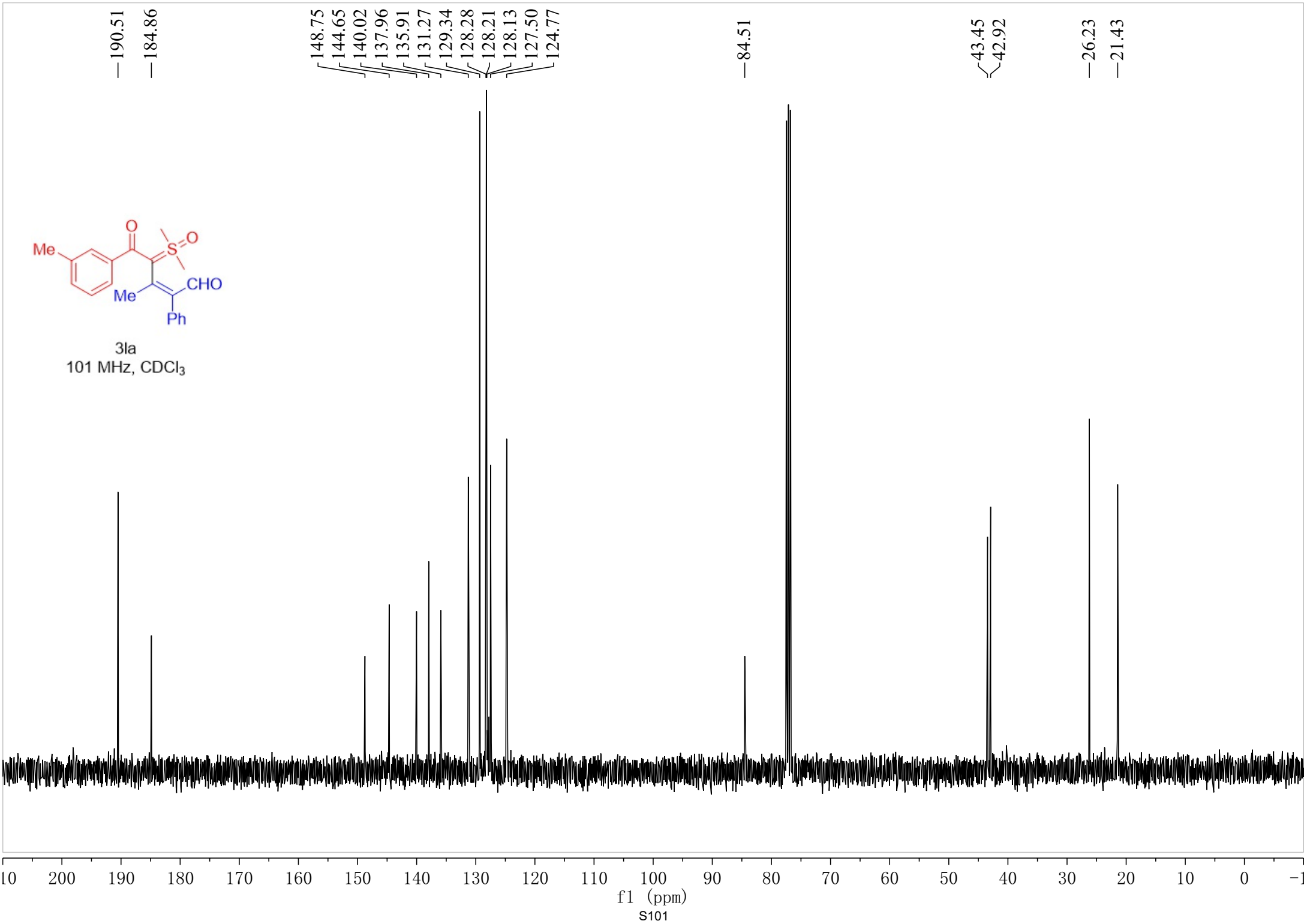

10.310
9.990
7.830
7.764
7.610
7.587
7.381
7.377
7.360
7.341
7.304
7.287
7.270
7.208
7.188
7.060
7.040
6.943
6.920
6.889
6.867
3.864
3.822
3.672
2.380
1.922
-0.000
O
S
O
MeO
Me
CHO
Ph
Z/E = 10:1
3ja
400 MHz, CDCl3
0.10
0.97
0.22
1.97
2.08
0.96
0.32
0.21
1.98
0.22
2.00
0.30
3.00
6.01
0.30
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

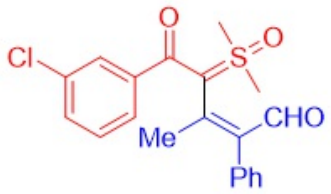

190.47
183.94
161.49
148.63
144.47
135.96
132.43
129.63
129.49
128.23
127.52
113.53
83.99
55.36
43.83
43.06
26.21
O
S
O
MeO
Me
CHO
Ph
3ja
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


10.282
9.967
7.605
7.555
7.534
7.526
7.521
7.520
7.516
7.505
7.499
7.495
7.484
7.479
7.473
7.463
7.458
7.453
7.382
7.379
7.374
7.366
7.361
7.357
7.346
7.343
7.341
7.337
7.316
7.312
7.309
7.300
7.294
7.287
7.284
7.279
7.275
7.134
7.129
7.118
7.114
7.110
6.996
6.992
6.987
6.979
6.975
6.972
6.966
3.670
2.413
1.918
O
S
O
Br
Me
CHO
Ph
Z/E = 10:1
3ka
400 MHz, CDCl3
0.09
0.98
0.22
0.24
4.01
2.09
1.17
0.22
1.97
6.00
0.29
3.00
f1 (ppm)

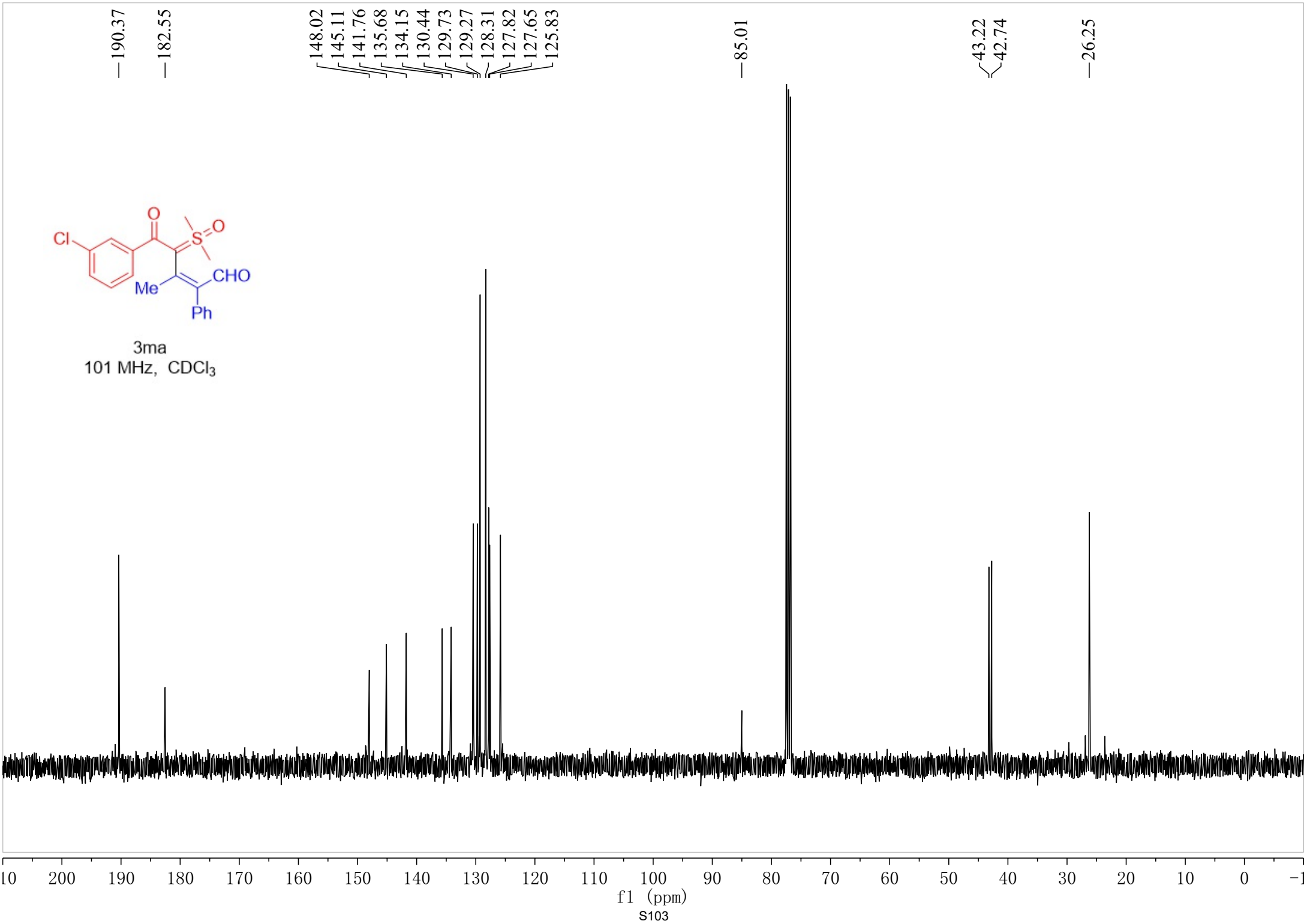

190.35
183.02
147.90
144.93
138.95
135.64
131.50
129.28
128.31
127.68
124.95
84.94
43.37
42.73
26.31
O
S
O
Br
Me
CHO
Ph
3ka
101 MHz, CDCl3
f1 (ppm)

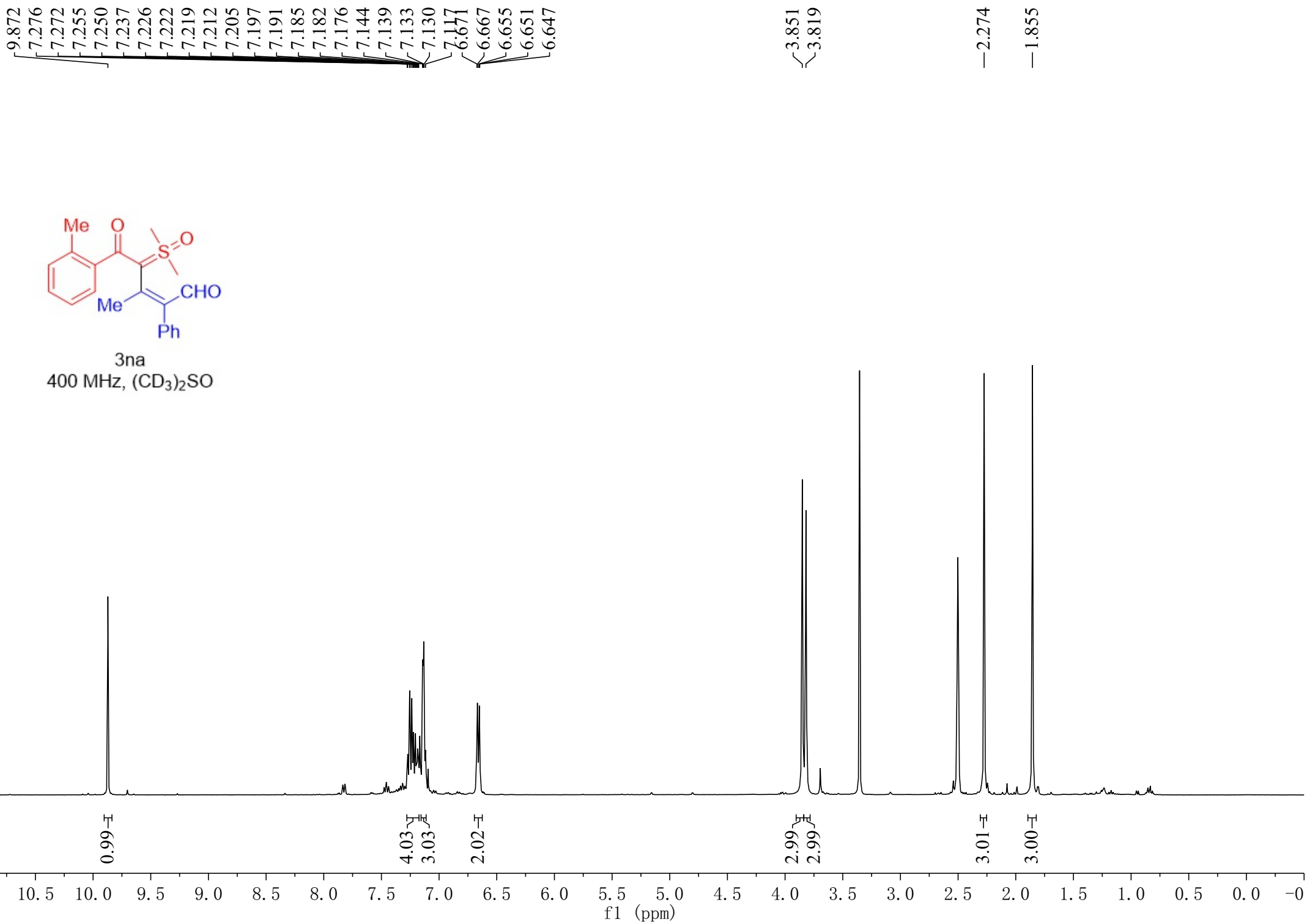

10.285
9.982
7.576
7.572
7.559
7.554
7.528
7.410
7.406
7.401
7.386
7.382
7.378
7.368
7.363
7.359
7.354
7.346
7.341
7.337
7.326
7.322
7.306
7.296
7.292
7.288
7.283
7.280
7.274
7.267
7.258
7.255
7.248
7.211
7.195
7.190
7.185
6.994
6.983
6.979
6.974
6.966
6.962
6.959
6.954
3.668
2.352
1.928
Me
O
S
O
CHO
Me
Ph
Z/E = 10:1
3la
400 MHz, CDCl3
0.08
0.93
0.31
4.13
2.21
1.18
1.97
6.00
0.31
3.00
3.32
f1 (ppm)

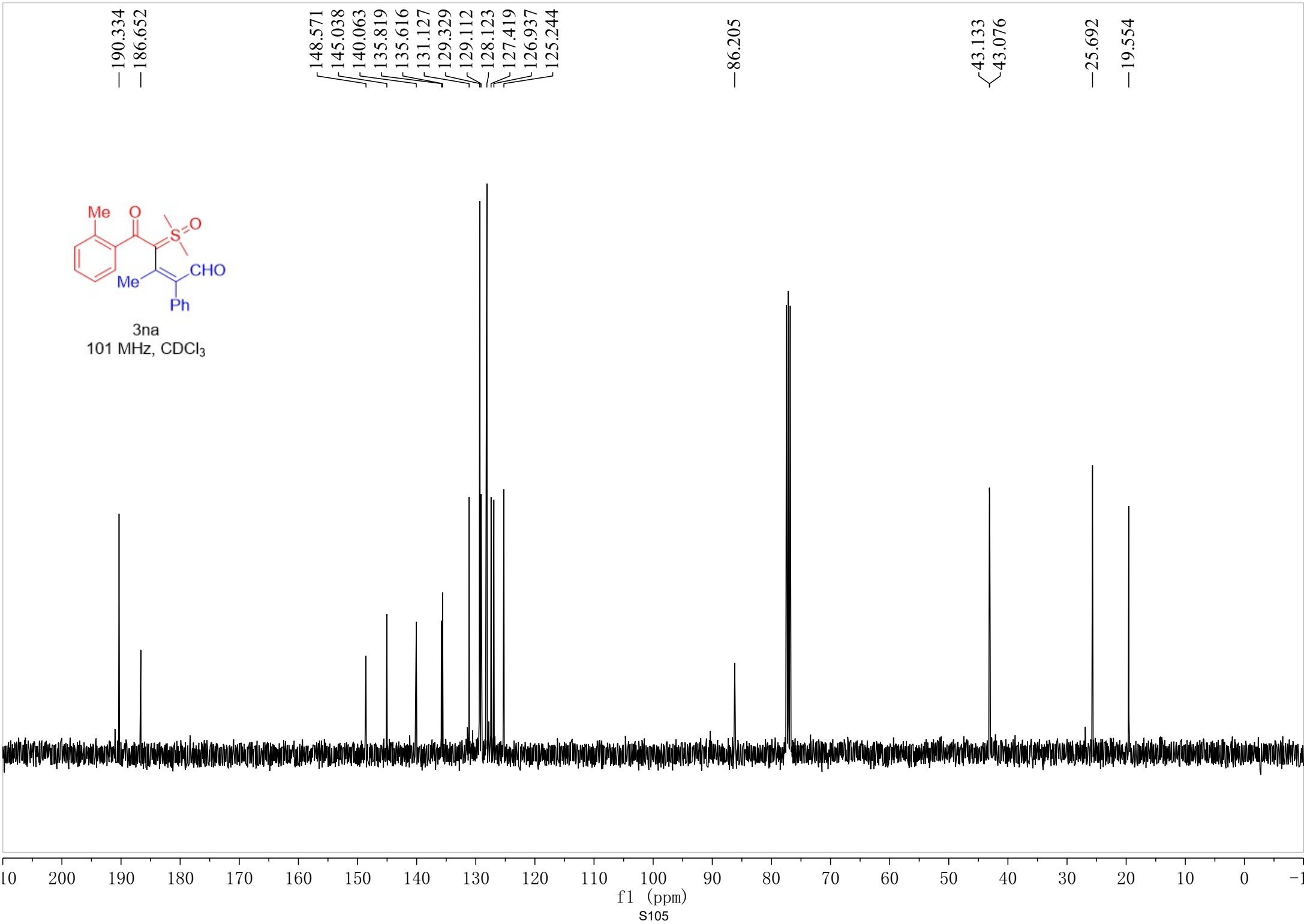

190.51
184.86
148.75
144.65
140.02
137.96
135.91
131.27
129.34
128.28
128.21
128.13
127.50
124.77
84.51
43.45
42.92
26.23
21.43
Me
O
S
O
CHO
Me
Ph
3la
101 MHz, CDCl3
f1 (ppm)

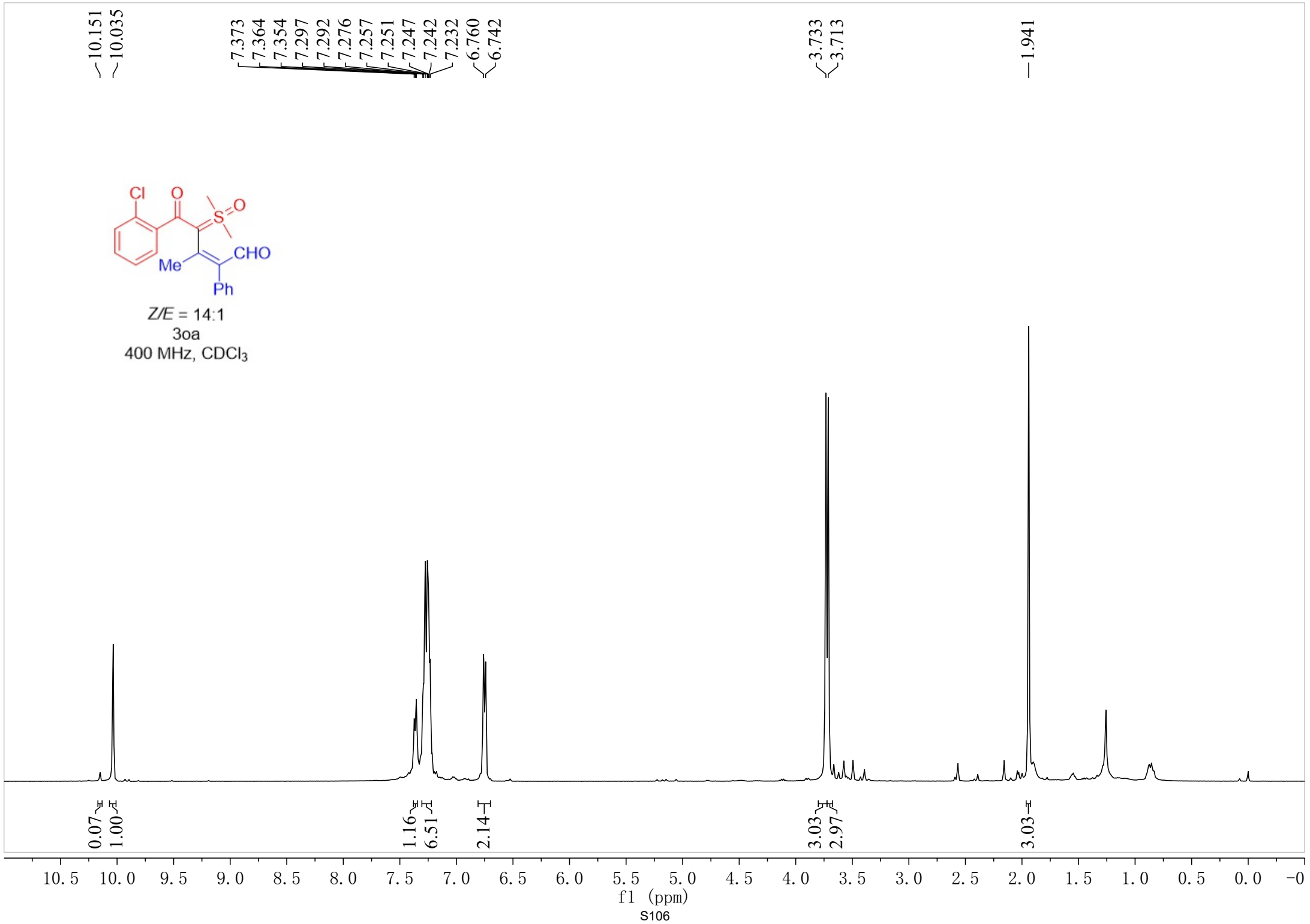


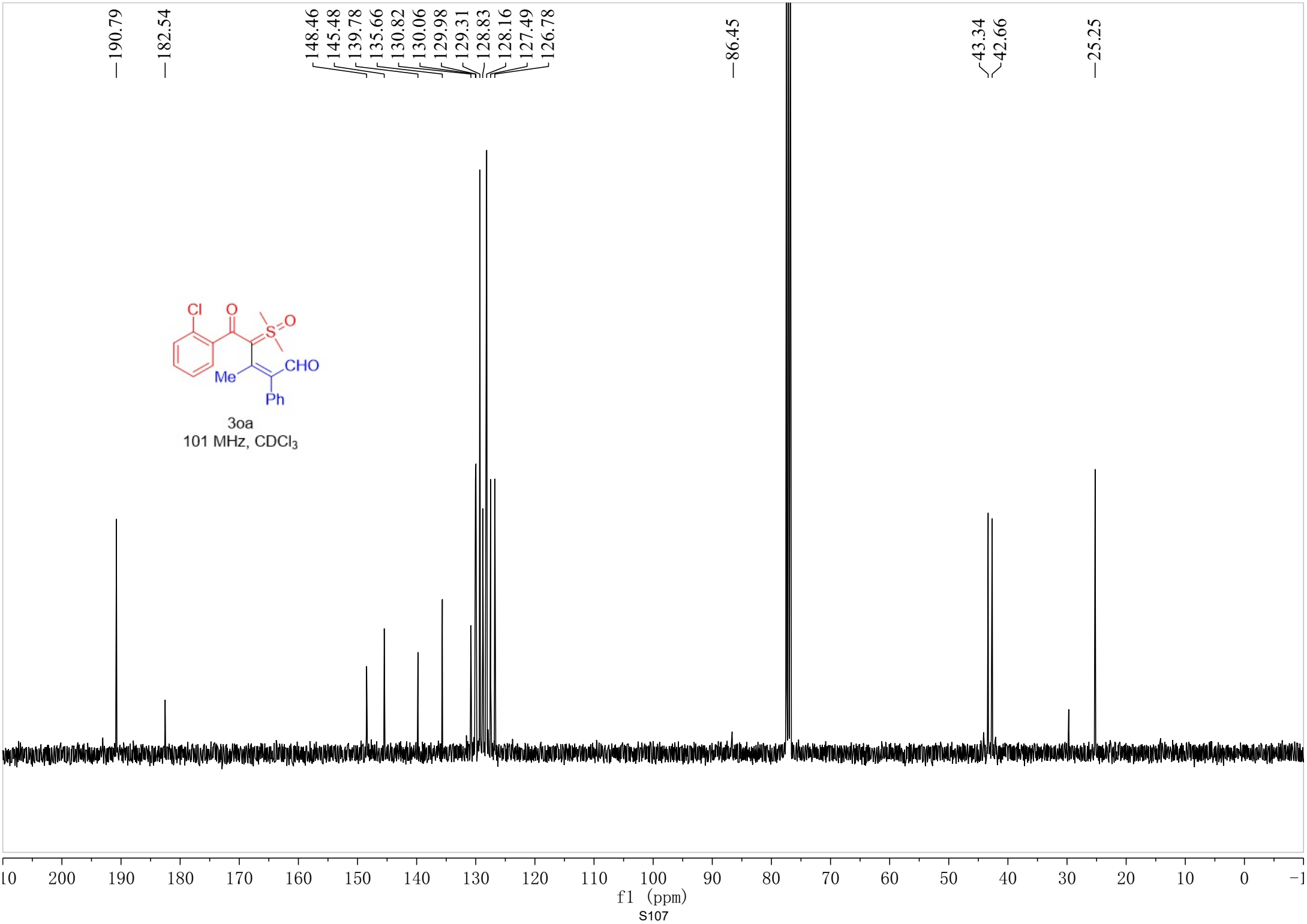
3ma
400 MHz, $(CD_3)_2SO$

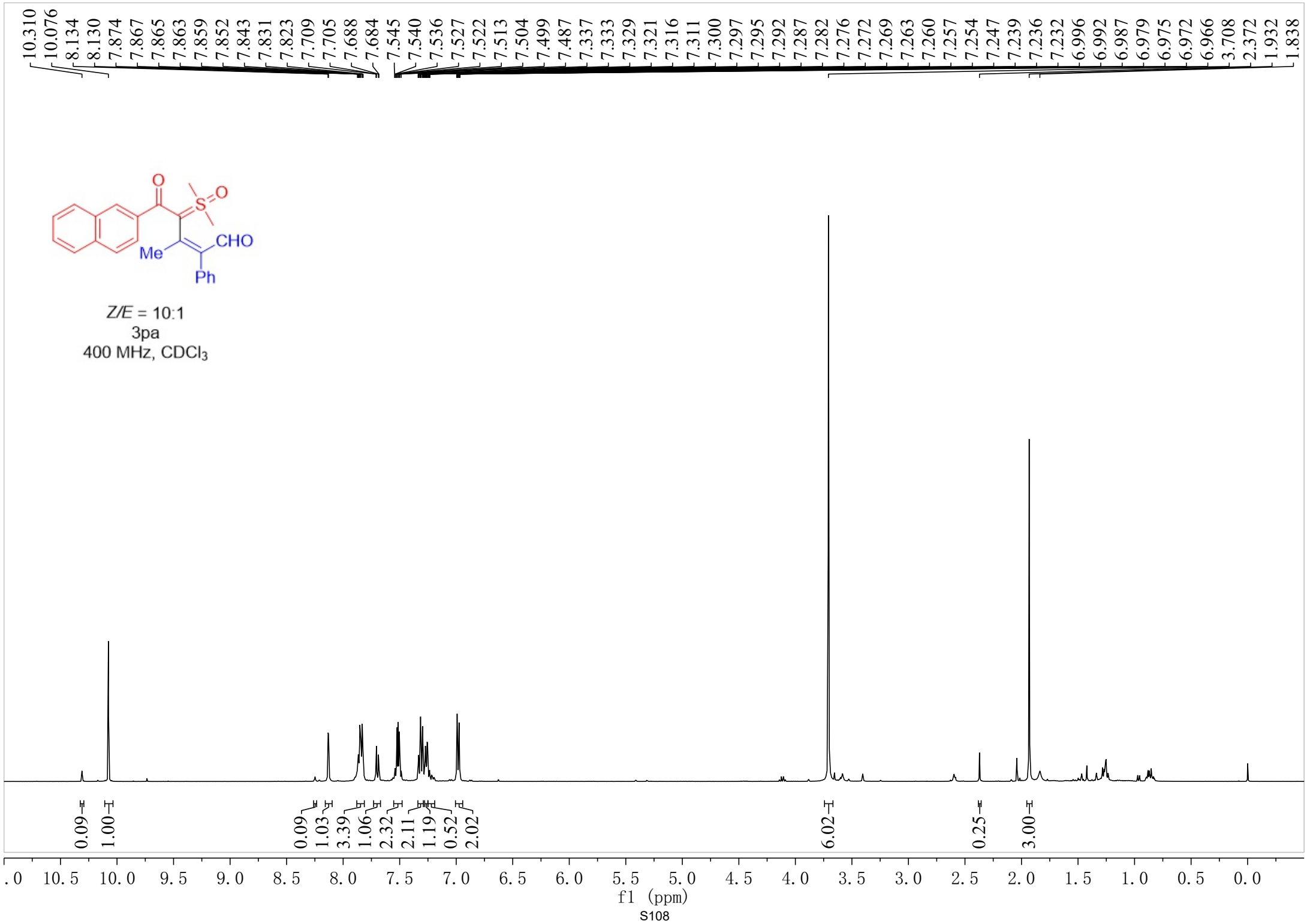

190.37
182.55
148.02
145.11
141.76
135.68
134.15
130.44
129.73
129.27
128.31
127.82
127.65
125.83
85.01
43.22
42.74
26.25
Cl
O
S
O
CHO
Me
Ph
3ma
101 MHz, CDCl3
f1 (ppm)

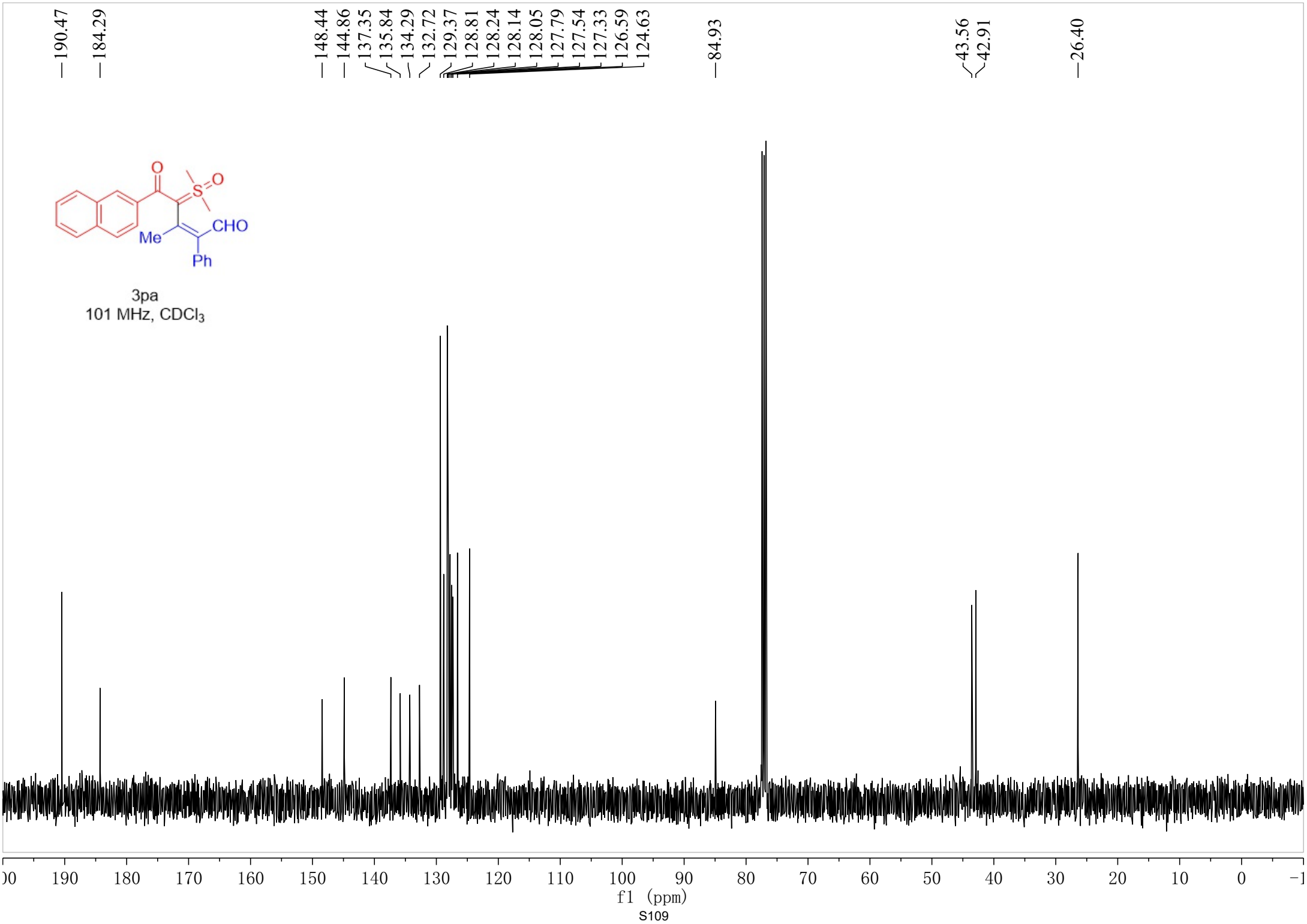

9.872
7.276
7.272
7.255
7.250
7.237
7.226
7.222
7.219
7.212
7.205
7.197
7.191
7.185
7.182
7.176
7.144
7.139
7.133
7.130
7.117
6.671
6.667
6.655
6.651
6.647
3.851
3.819
2.274
1.855
Me
O
S
O
CHO
Me
Ph
3na
400 MHz, (CD3)2SO
0.99
4.03
3.03
2.02
2.99
2.99
3.01
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

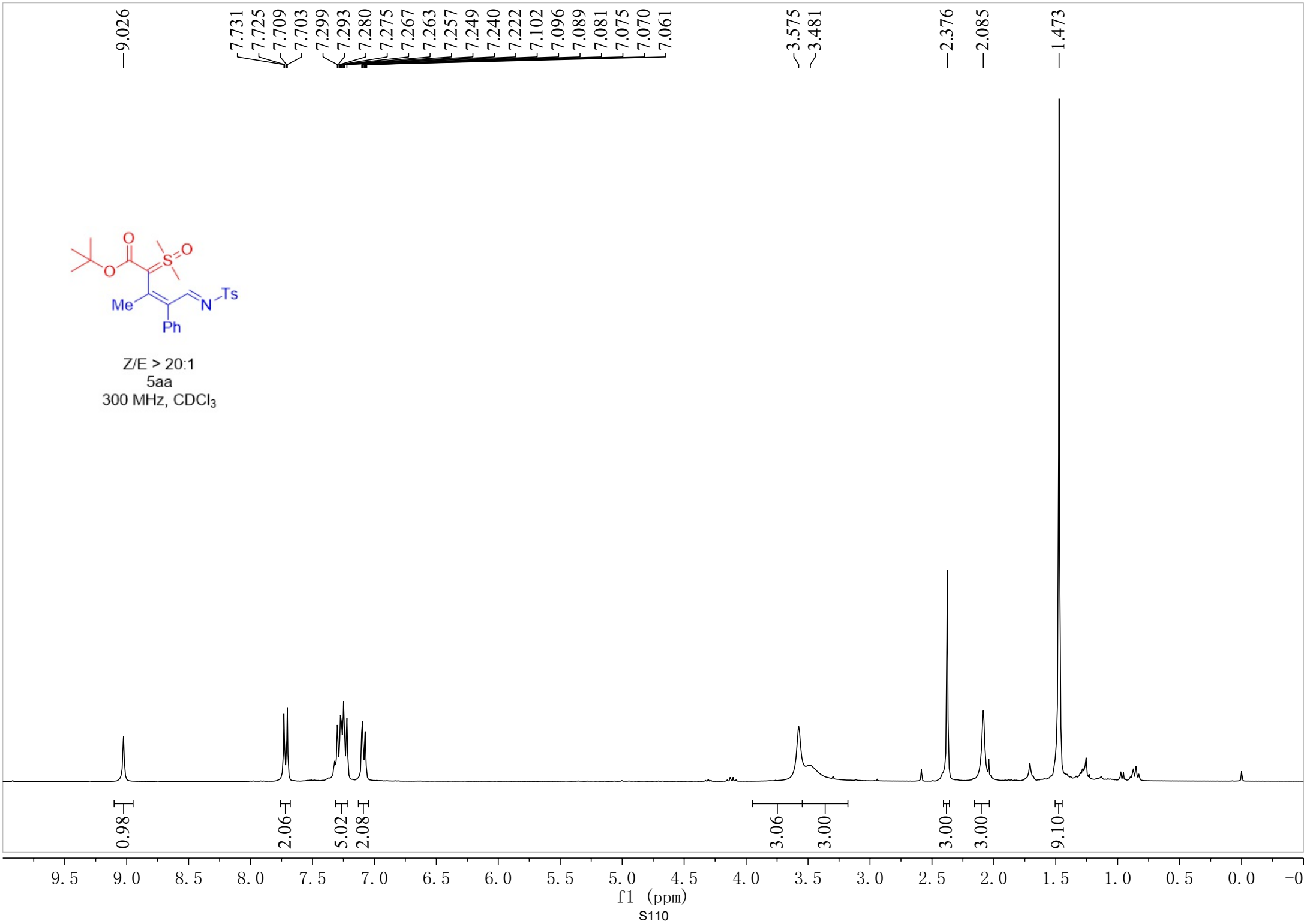

190.334
186.652
148.571
145.038
140.063
135.819
135.616
131.127
129.329
129.112
128.123
127.419
126.937
125.244
86.205
43.133
43.076
25.692
19.554
Me
O
S
O
Me
CHO
Ph
3na
101 MHz, CDCl3
f1 (ppm)

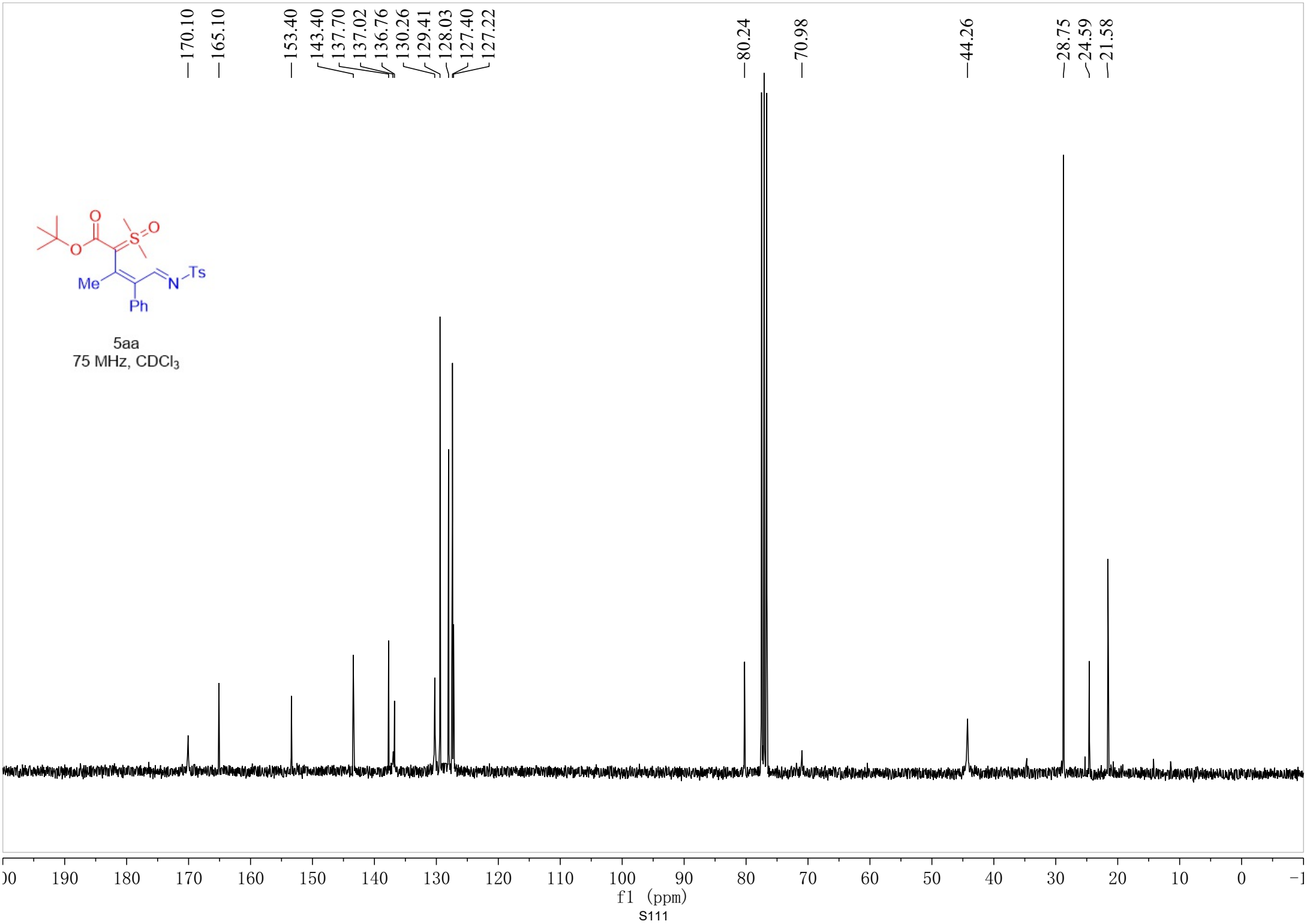

10.151
10.035
7.373
7.364
7.354
7.297
7.292
7.276
7.257
7.251
7.247
7.242
7.232
6.760
6.742
3.733
3.713
1.941
Cl
O
S
O
CHO
Me
Ph
Z/E = 14:1
3oa
400 MHz, CDCl3
0.07
1.00
1.16
6.51
2.14
3.03
2.97
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

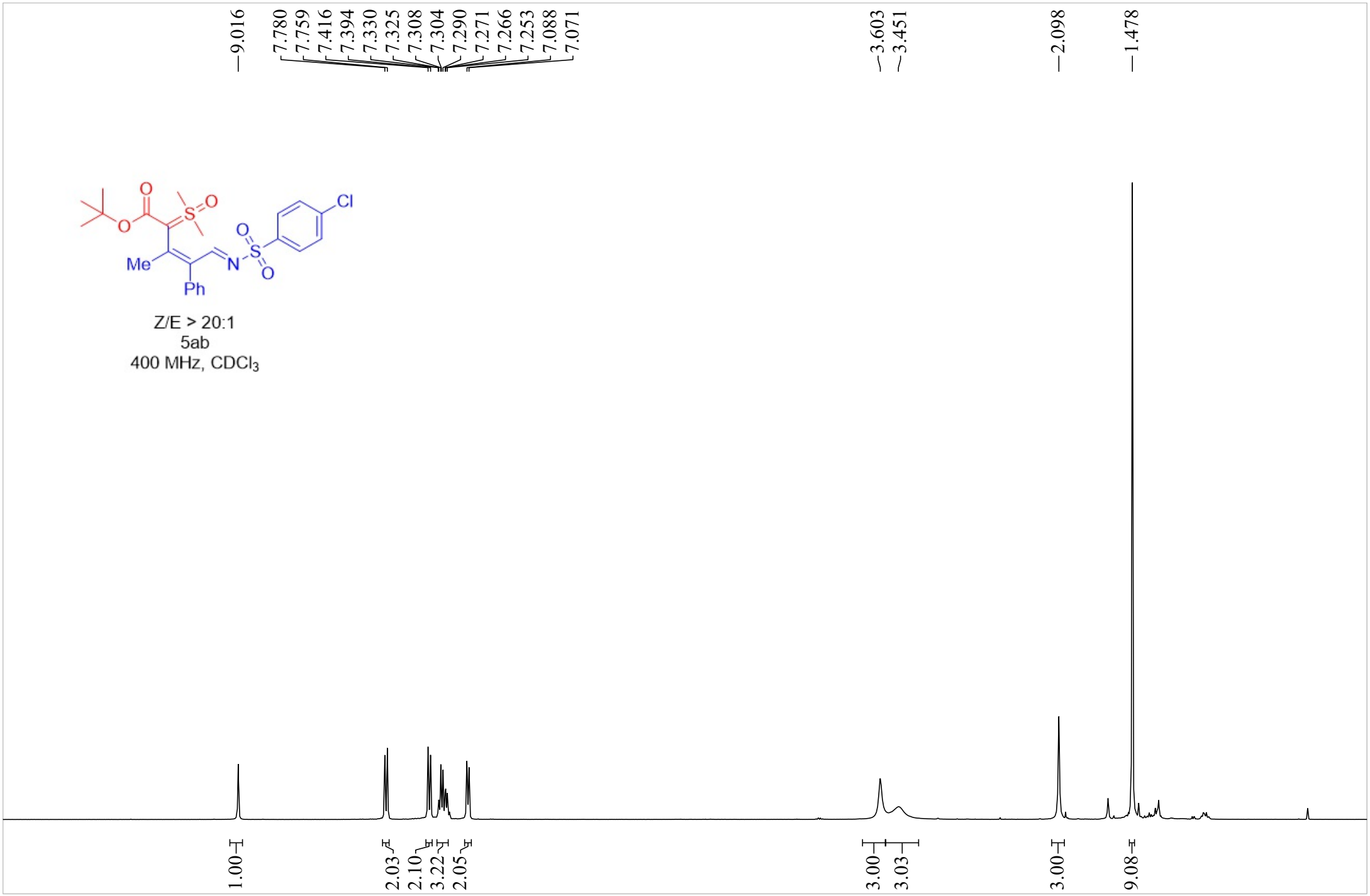

190.79
182.54
148.46
145.48
139.78
135.66
130.82
130.06
129.98
129.31
128.83
128.16
127.49
126.78
86.45
43.34
42.66
25.25
Cl
O
S
O
CHO
Me
Ph
3oa
101 MHz, CDCl3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

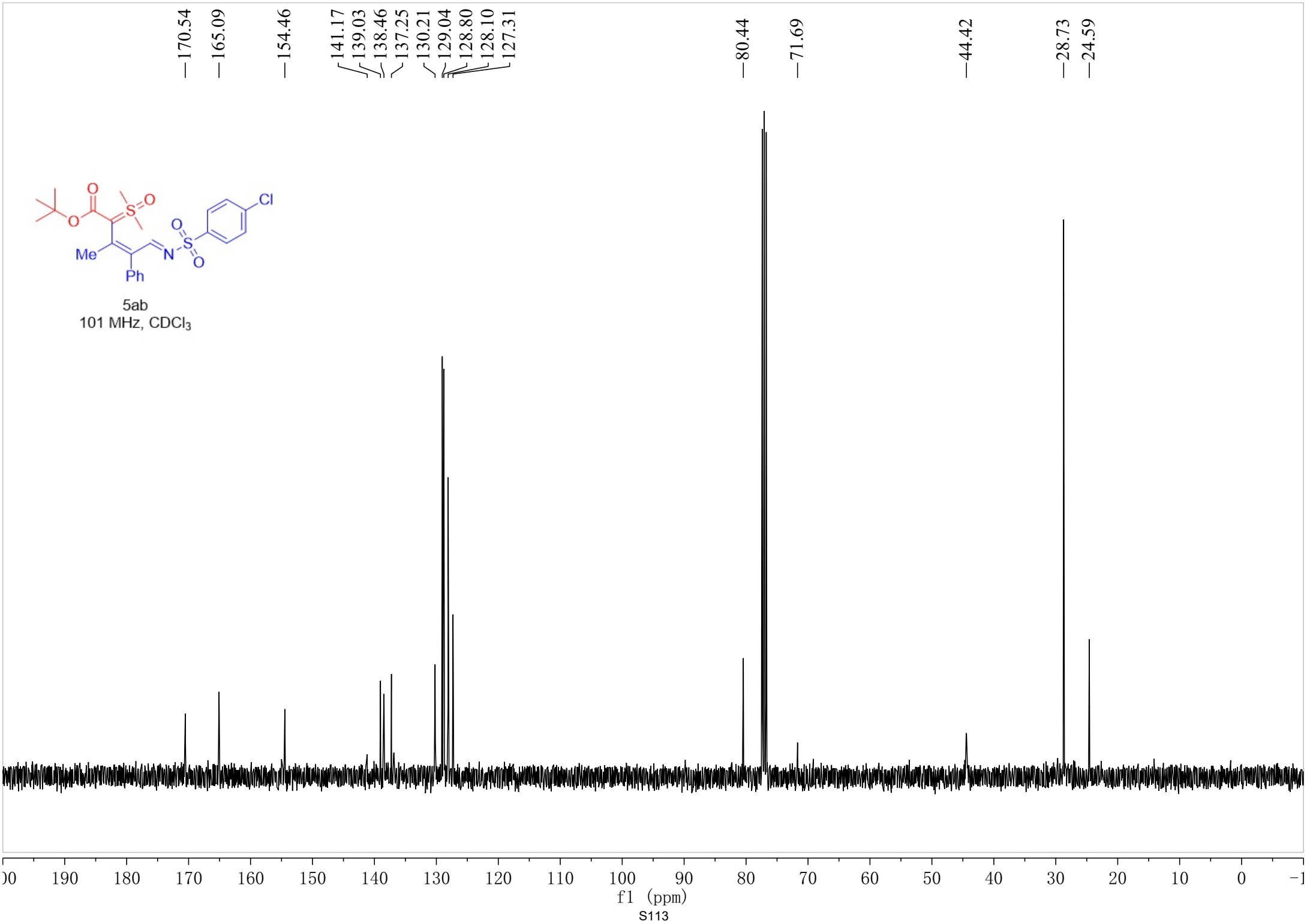

10.310
10.076
8.134
8.130
7.874
7.867
7.865
7.863
7.859
7.852
7.843
7.831
7.823
7.709
7.705
7.688
7.684
7.545
7.540
7.536
7.527
7.522
7.513
7.504
7.499
7.487
7.337
7.333
7.329
7.321
7.316
7.311
7.300
7.297
7.295
7.292
7.287
7.282
7.276
7.272
7.269
7.263
7.260
7.257
7.254
7.247
7.239
7.236
7.232
6.996
6.992
6.987
6.979
6.975
6.972
6.966
3.708
2.372
1.932
1.838
O
S
O
CHO
Me
Ph
Z/E = 10:1
3pa
400 MHz, CDCl3
0.09
1.00
0.09
1.03
3.39
1.06
2.32
2.11
1.19
0.52
2.02
6.02
0.25
3.00
f1 (ppm)

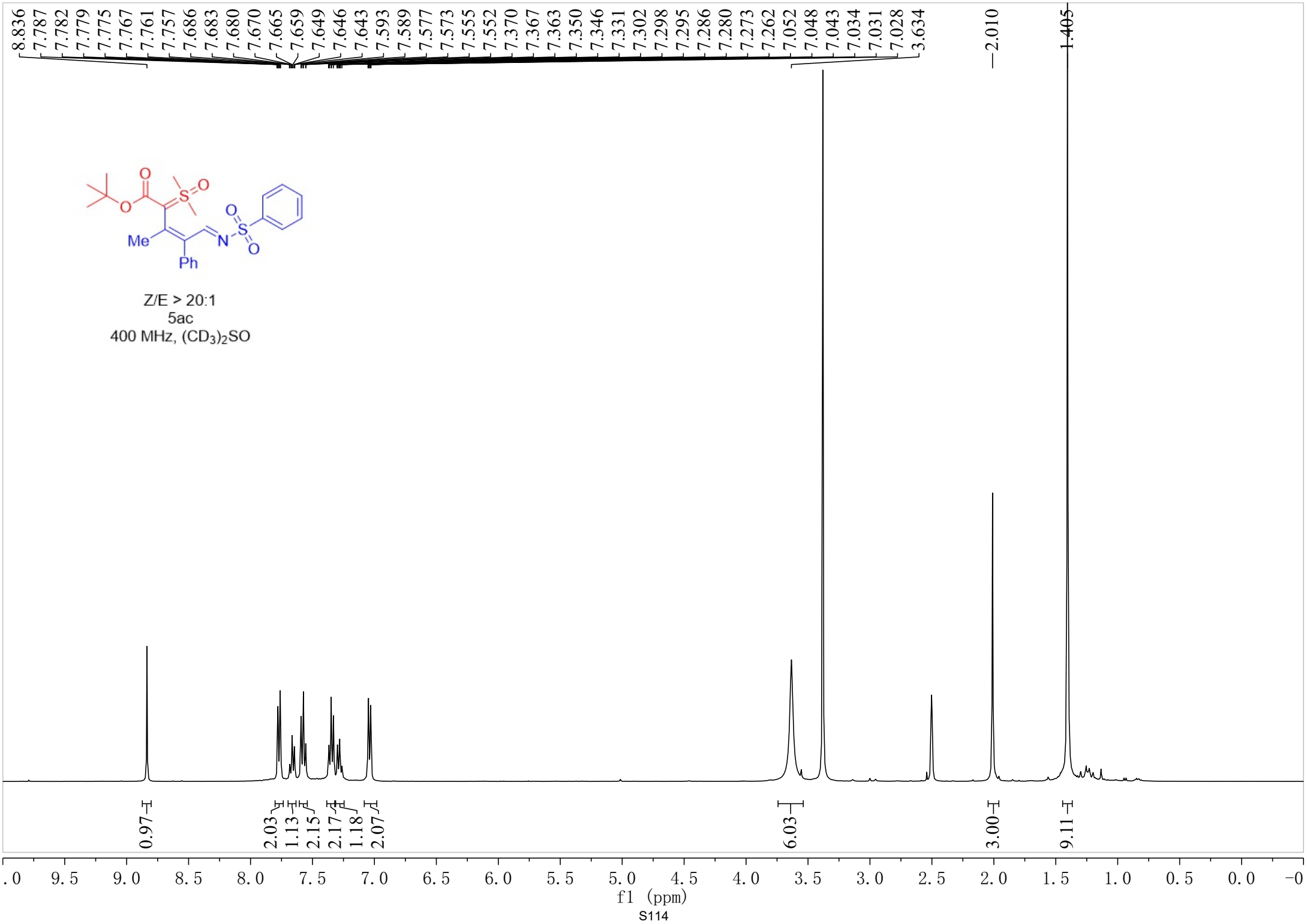

190.47
184.29
148.44
144.86
137.35
135.84
134.29
132.72
129.37
128.81
128.24
128.14
128.05
127.79
127.54
127.33
126.59
124.63
84.93
43.56
42.91
26.40
O
S
O
CHO
Me
Ph
3pa
101 MHz, CDCl3
f1 (ppm)

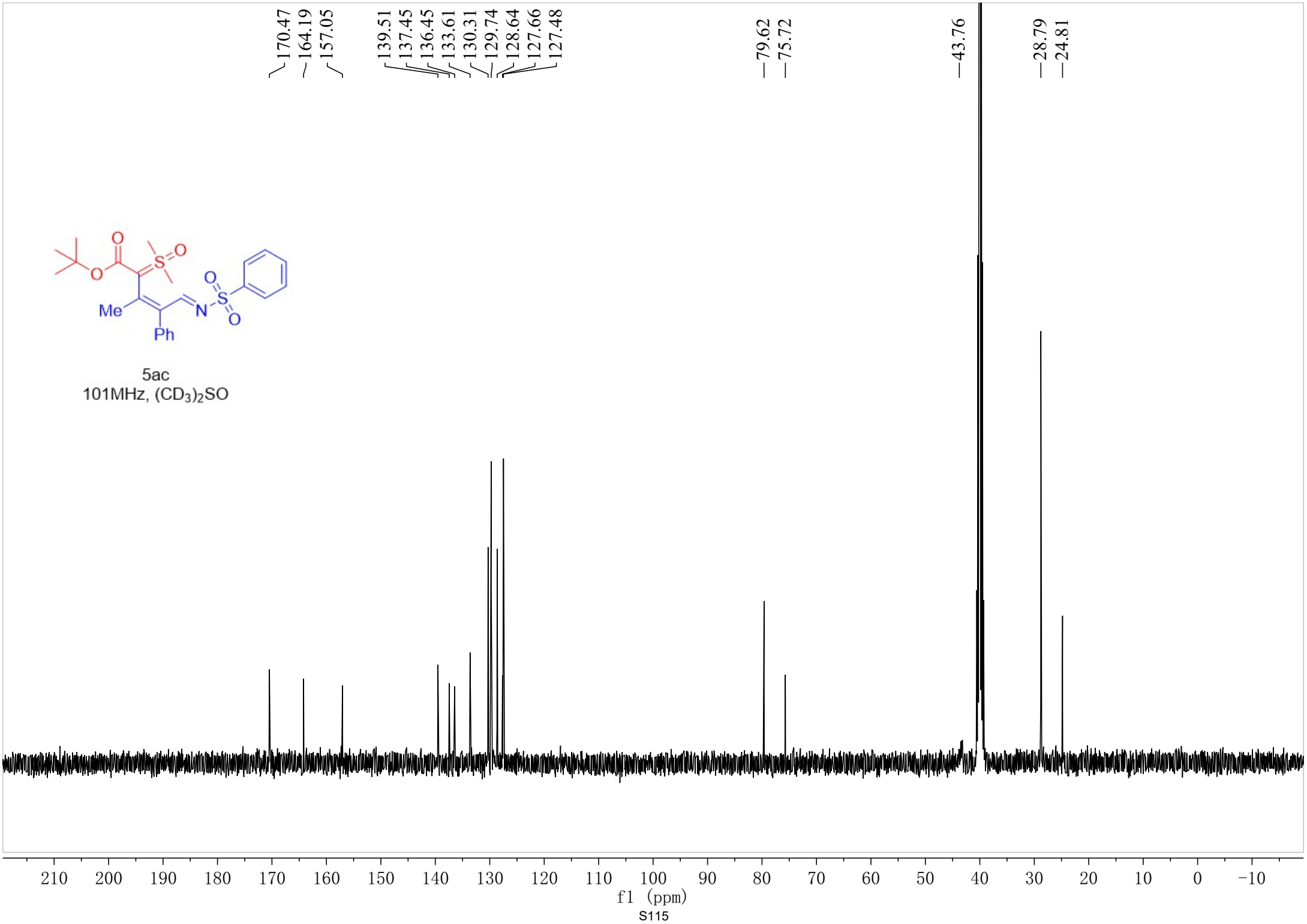

9.026
7.731
7.725
7.709
7.703
7.299
7.293
7.280
7.275
7.267
7.263
7.257
7.249
7.240
7.222
7.102
7.096
7.089
7.081
7.075
7.070
7.061
3.575
3.481
2.376
2.085
1.473
Me
Ph
N
Ts
Z/E > 20:1
5aa
300 MHz, CDCl3
0.98
2.06
5.02
2.08
3.06
3.00
3.00
3.00
9.10
f1 (ppm)

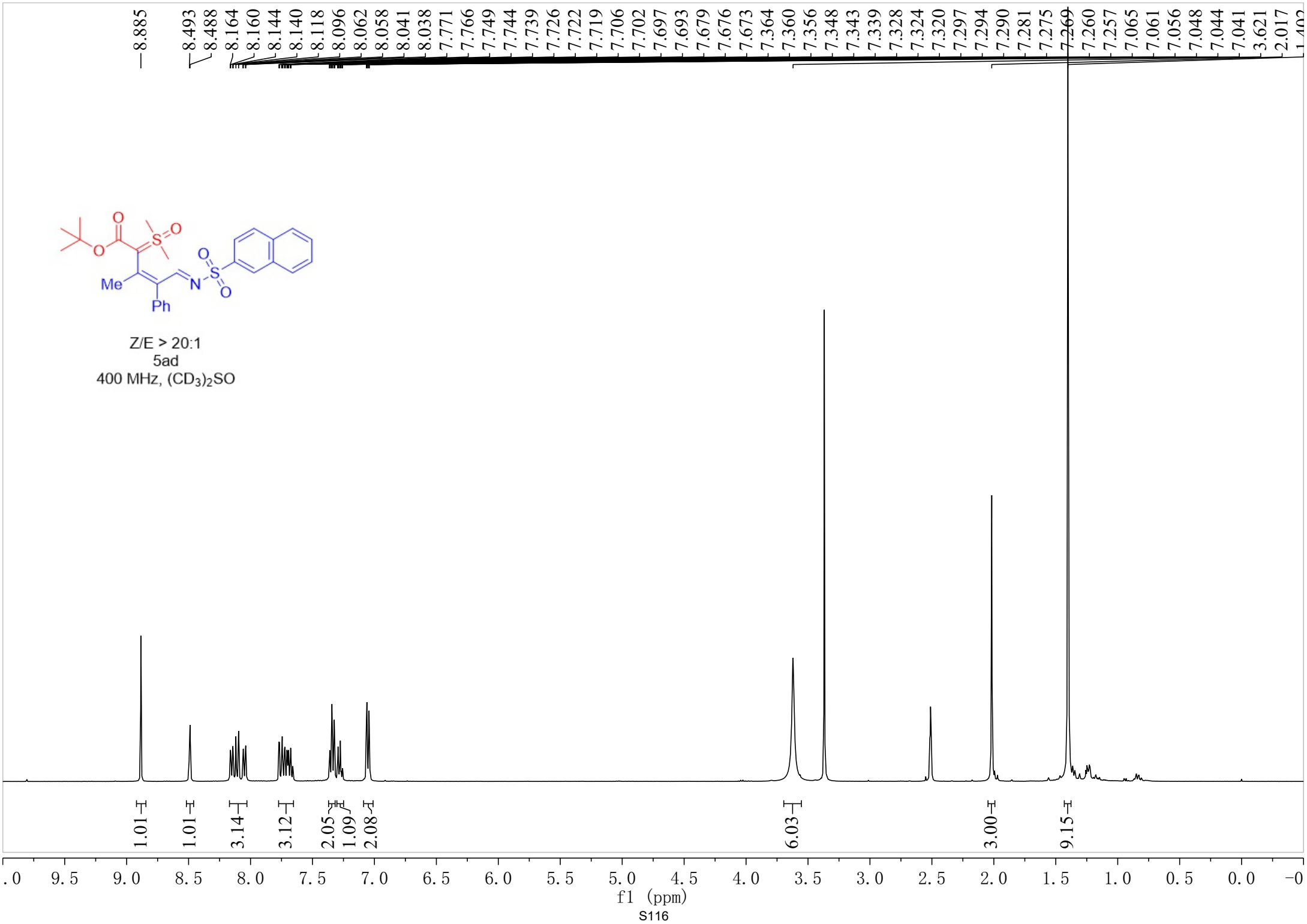

170.10
165.10
153.40
143.40
137.70
137.02
136.76
130.26
129.41
128.03
127.40
127.22
80.24
70.98
44.26
28.75
24.59
21.58
O
O
S
O
Me
N
Ts
Ph
5aa
75 MHz, CDCl3
f1 (ppm)

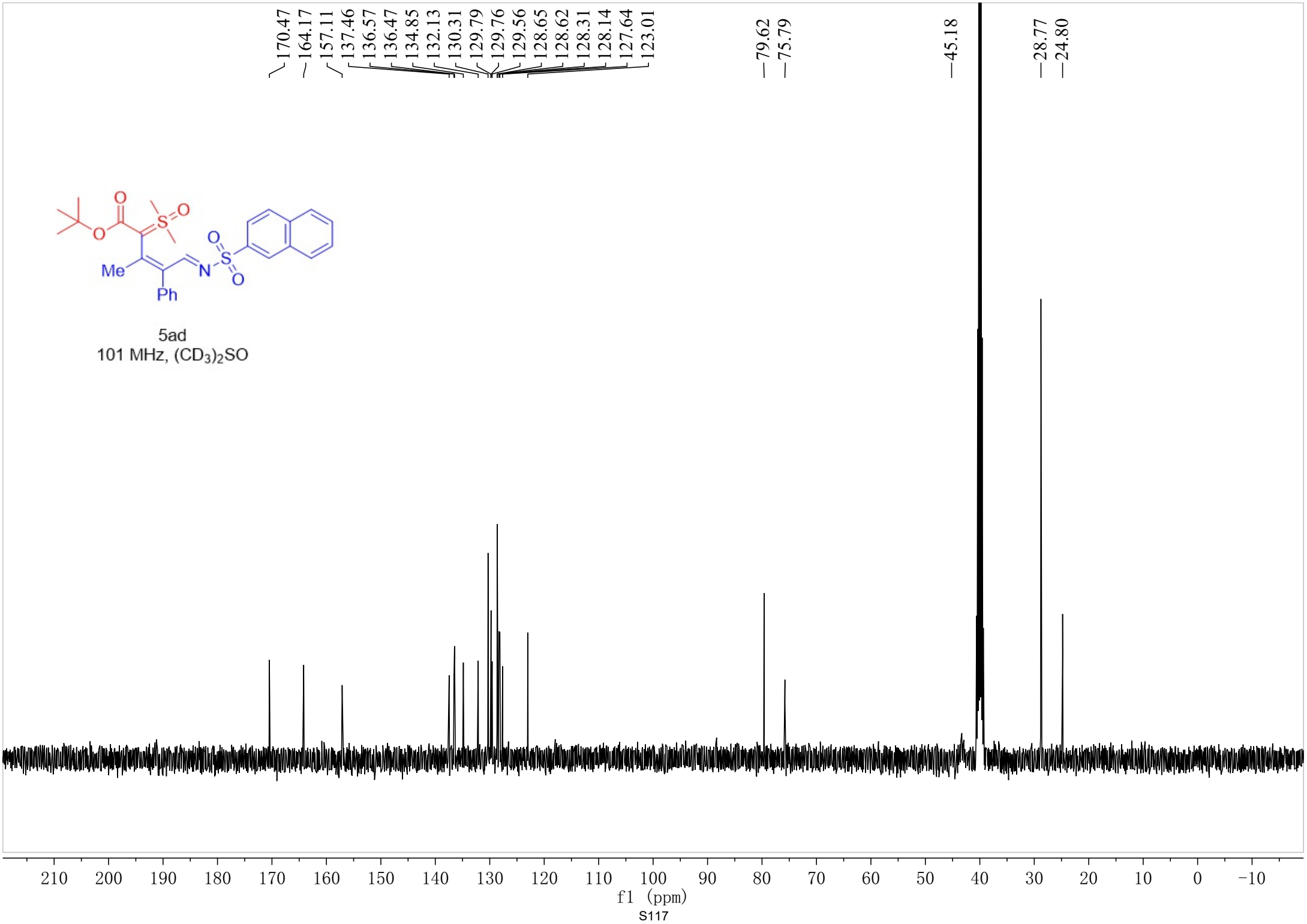

9.016
7.780
7.759
7.416
7.394
7.330
7.325
7.308
7.304
7.290
7.271
7.266
7.253
7.088
7.071
3.603
3.451
2.098
1.478
Z/E > 20:1
5ab
400 MHz, CDCl3
1.00
2.03
2.10
3.22
2.05
3.00
3.03
3.00
9.08
f1 (ppm)

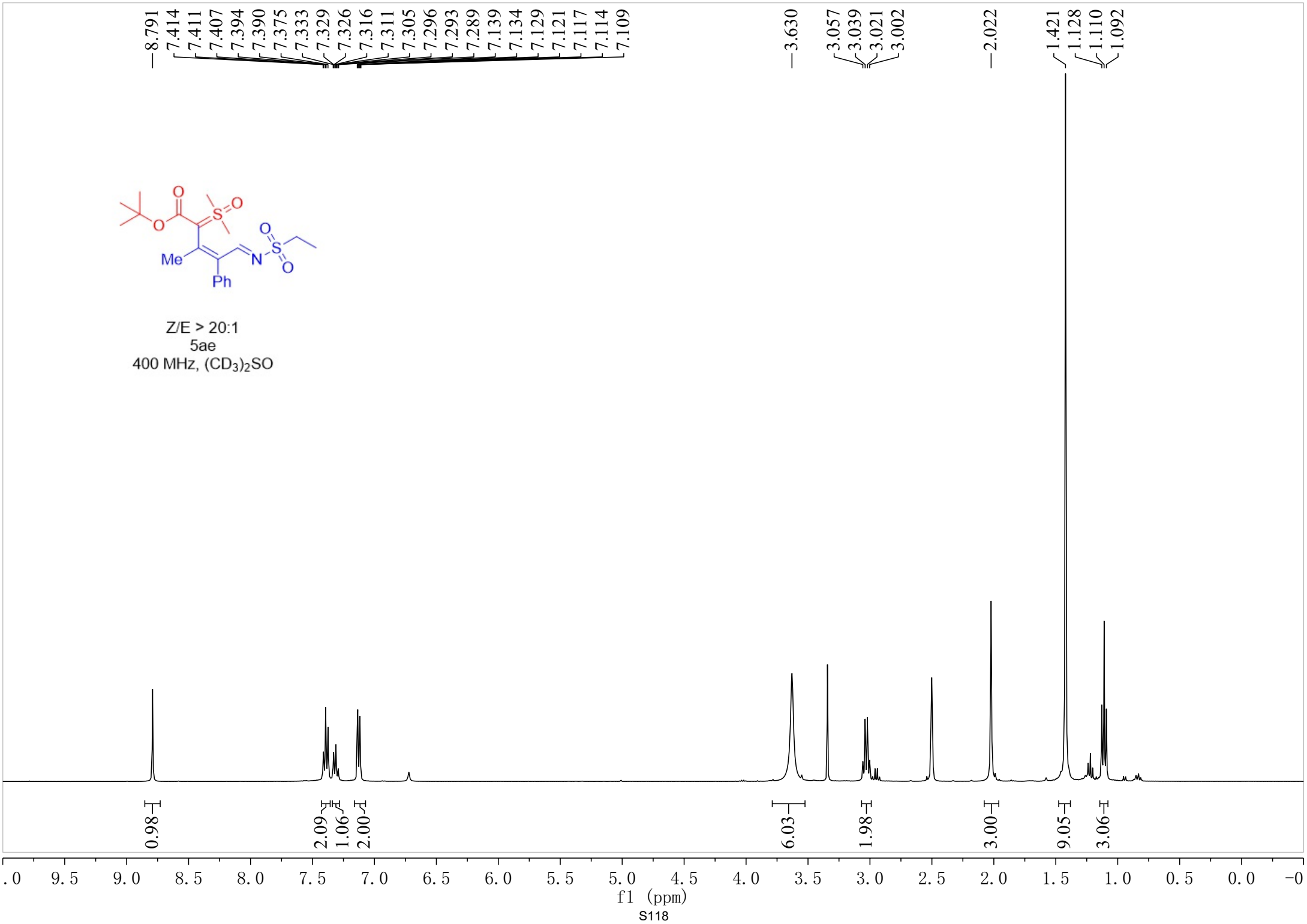

170.54
165.09
154.46
141.17
139.03
138.46
137.25
130.21
129.04
128.80
128.10
127.31
80.44
71.69
44.42
28.73
24.59
5ab
101 MHz, CDCl3
f1 (ppm)

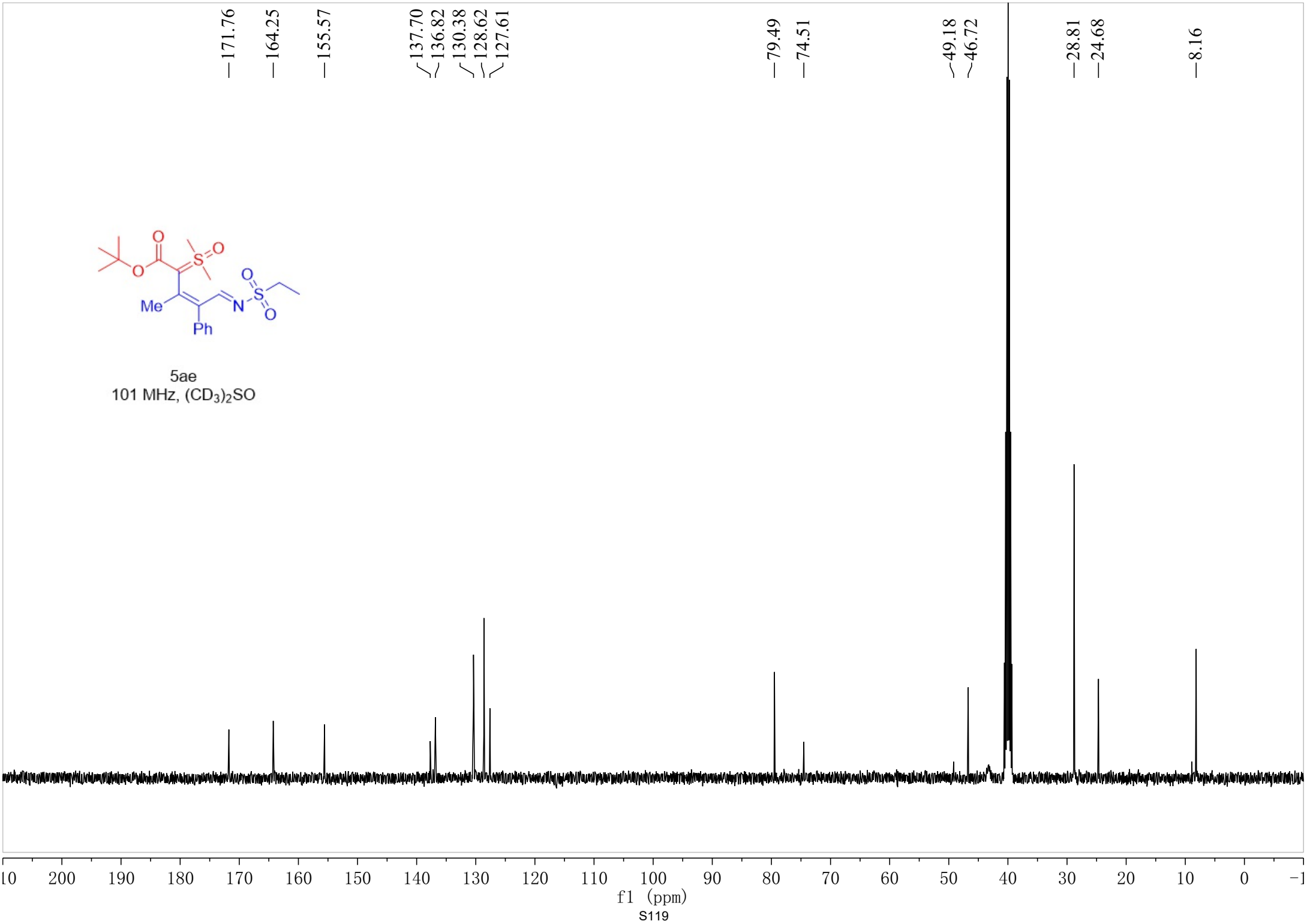

8.836
7.787
7.782
7.779
7.775
7.767
7.761
7.757
7.686
7.683
7.680
7.670
7.665
7.659
7.649
7.646
7.643
7.593
7.589
7.577
7.573
7.555
7.552
7.370
7.367
7.363
7.350
7.346
7.331
7.302
7.298
7.295
7.286
7.280
7.273
7.262
7.052
7.048
7.043
7.034
7.031
7.028
3.634
2.010
1.405
Me
Ph
Z/E > 20:1
5ac
400 MHz, (CD3)2SO
0.97
2.03
1.13
2.15
2.17
1.18
2.07
6.03
3.00
9.11
f1 (ppm)

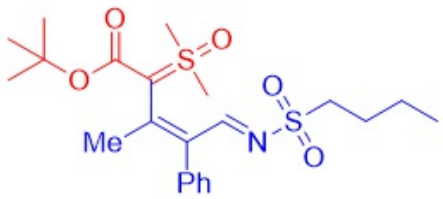

170.47
164.19
157.05
139.51
137.45
136.45
133.61
130.31
129.74
128.64
127.66
127.48
79.62
75.72
43.76
28.79
24.81
Me
Ph
5ac
101MHz, (CD3)2SO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.885
8.493
8.488
8.164
8.160
8.144
8.140
8.118
8.096
8.062
8.058
8.041
8.038
7.771
7.766
7.749
7.744
7.739
7.726
7.722
7.719
7.706
7.702
7.697
7.693
7.679
7.676
7.673
7.364
7.360
7.356
7.348
7.343
7.339
7.328
7.324
7.320
7.297
7.294
7.290
7.281
7.275
7.269
7.260
7.257
7.065
7.061
7.056
7.048
7.044
7.041
3.621
2.017
1.402
Me
Ph
N
Z/E > 20:1
5ad
400 MHz, (CD3)2SO
1.01
1.01
3.14
3.12
2.05
1.09
2.08
6.03
3.00
9.15
f1 (ppm)

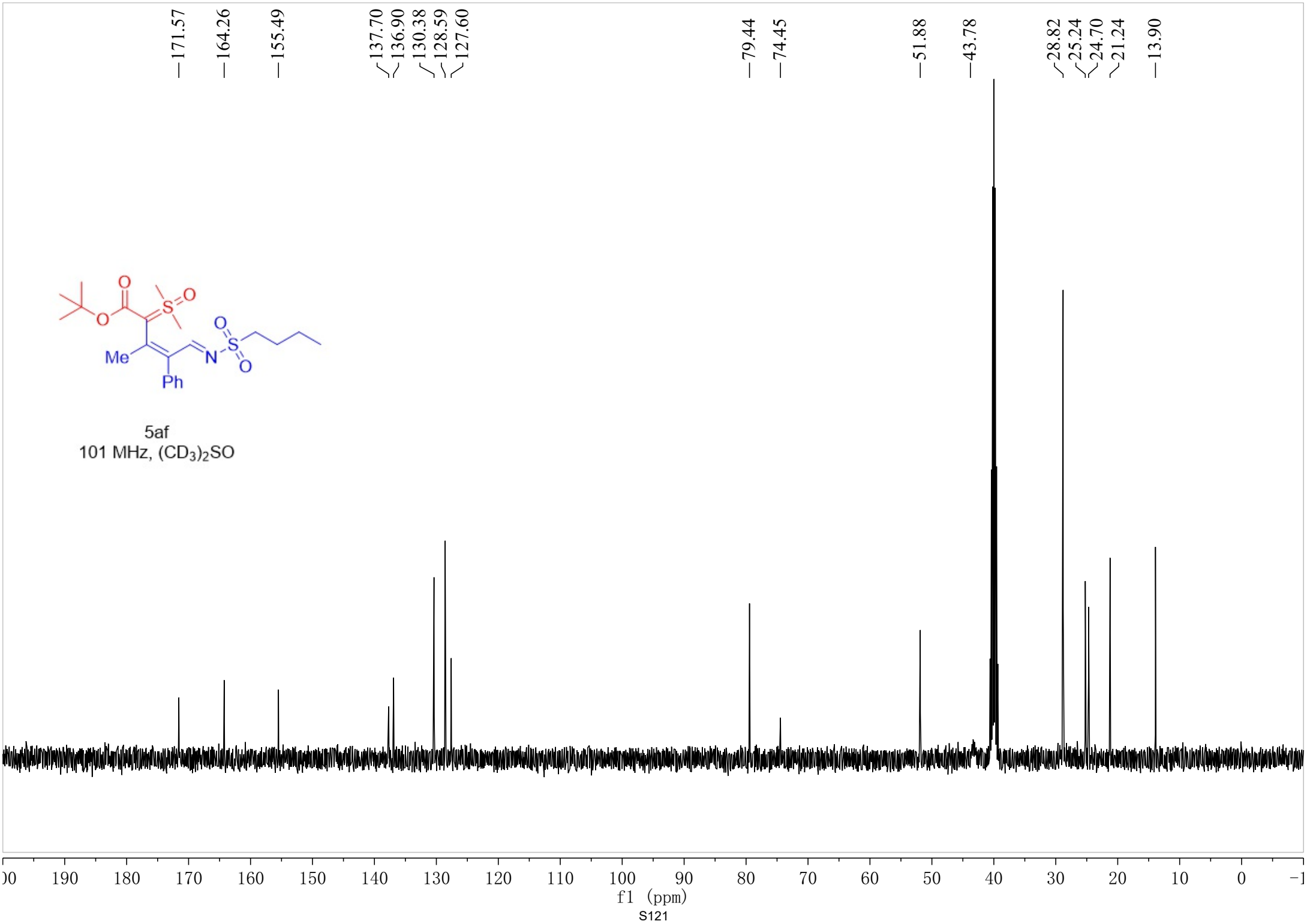

170.47
164.17
157.11
137.46
136.57
136.47
134.85
132.13
130.31
129.79
129.76
129.56
128.65
128.62
128.31
128.14
127.64
123.01
79.62
75.79
45.18
28.77
24.80
Me
Ph
5ad
101 MHz, (CD3)2SO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

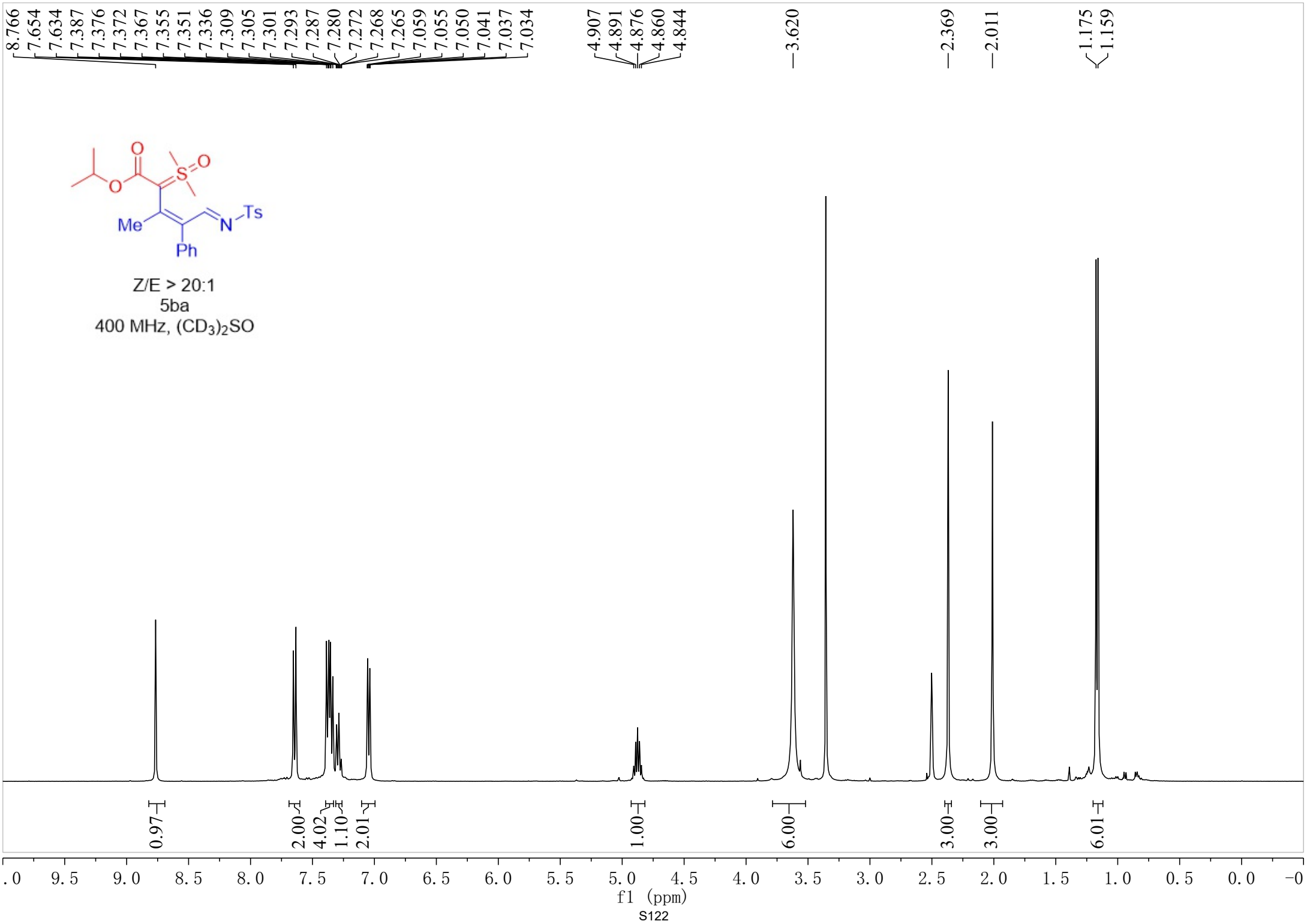

8.791
7.414
7.411
7.407
7.394
7.390
7.375
7.333
7.329
7.326
7.316
7.311
7.305
7.296
7.293
7.289
7.139
7.134
7.129
7.121
7.117
7.114
7.109
3.630
3.057
3.039
3.021
3.002
2.022
1.421
1.128
1.110
1.092
Me
Ph
Z/E > 20:1
5ae
400 MHz, (CD3)2SO
0.98
2.09
1.06
2.00
6.03
1.98
3.00
9.05
3.06
f1 (ppm)

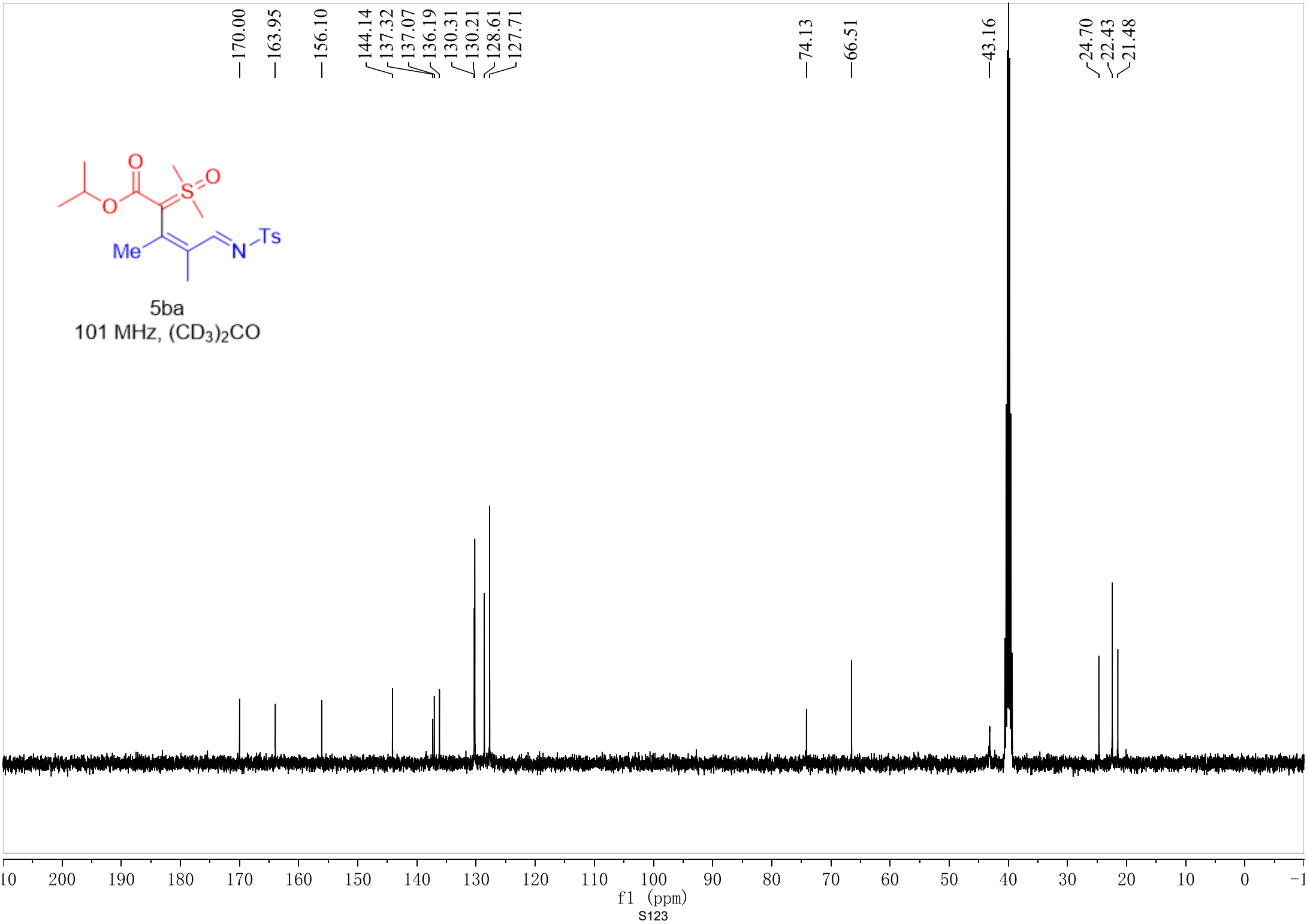

171.76
164.25
155.57
137.70
136.82
130.38
128.62
127.61
79.49
74.51
49.18
46.72
28.81
24.68
8.16
Me
Ph
N
O
S
5ae
101 MHz, (CD3)2SO
f1 (ppm)

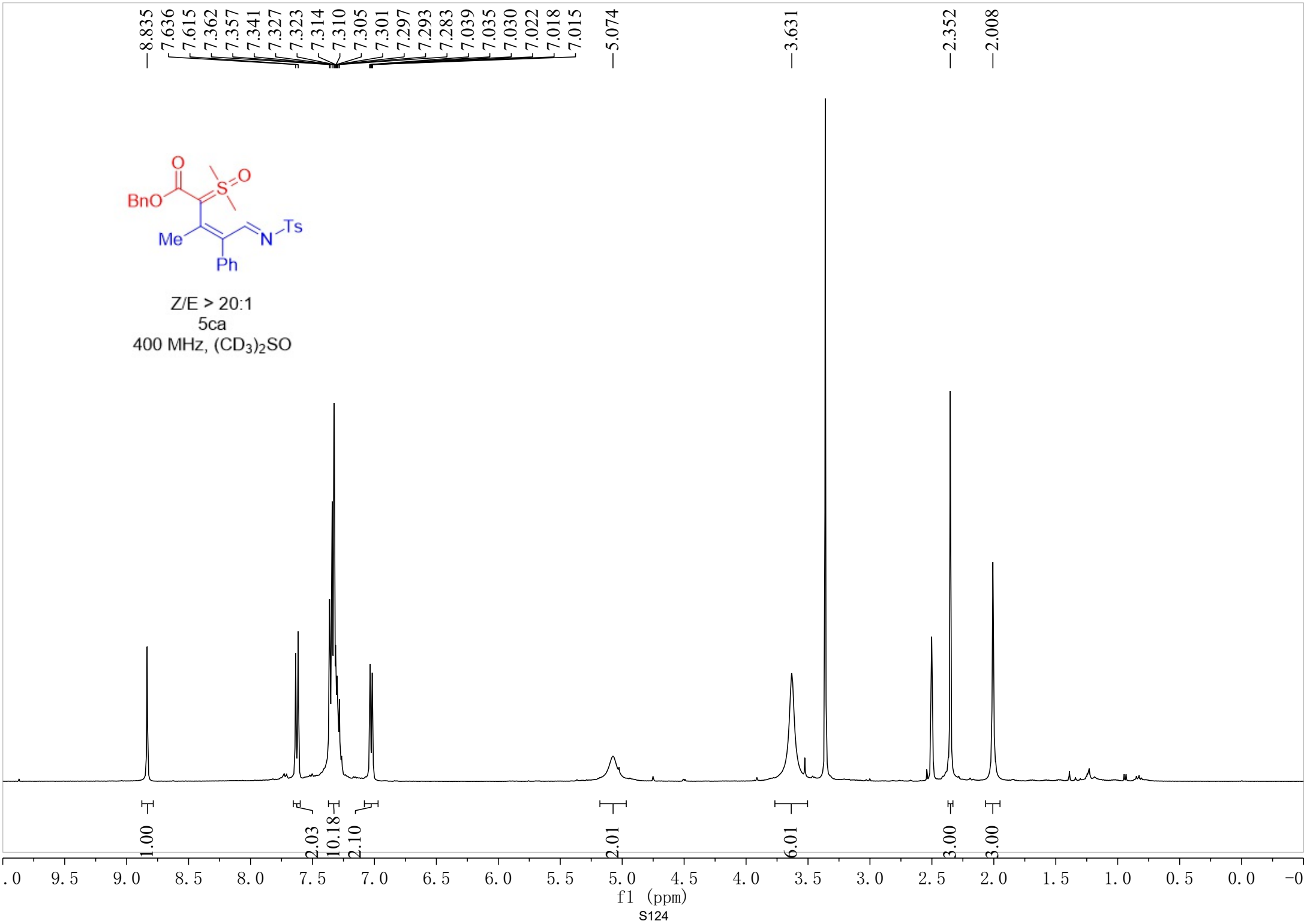


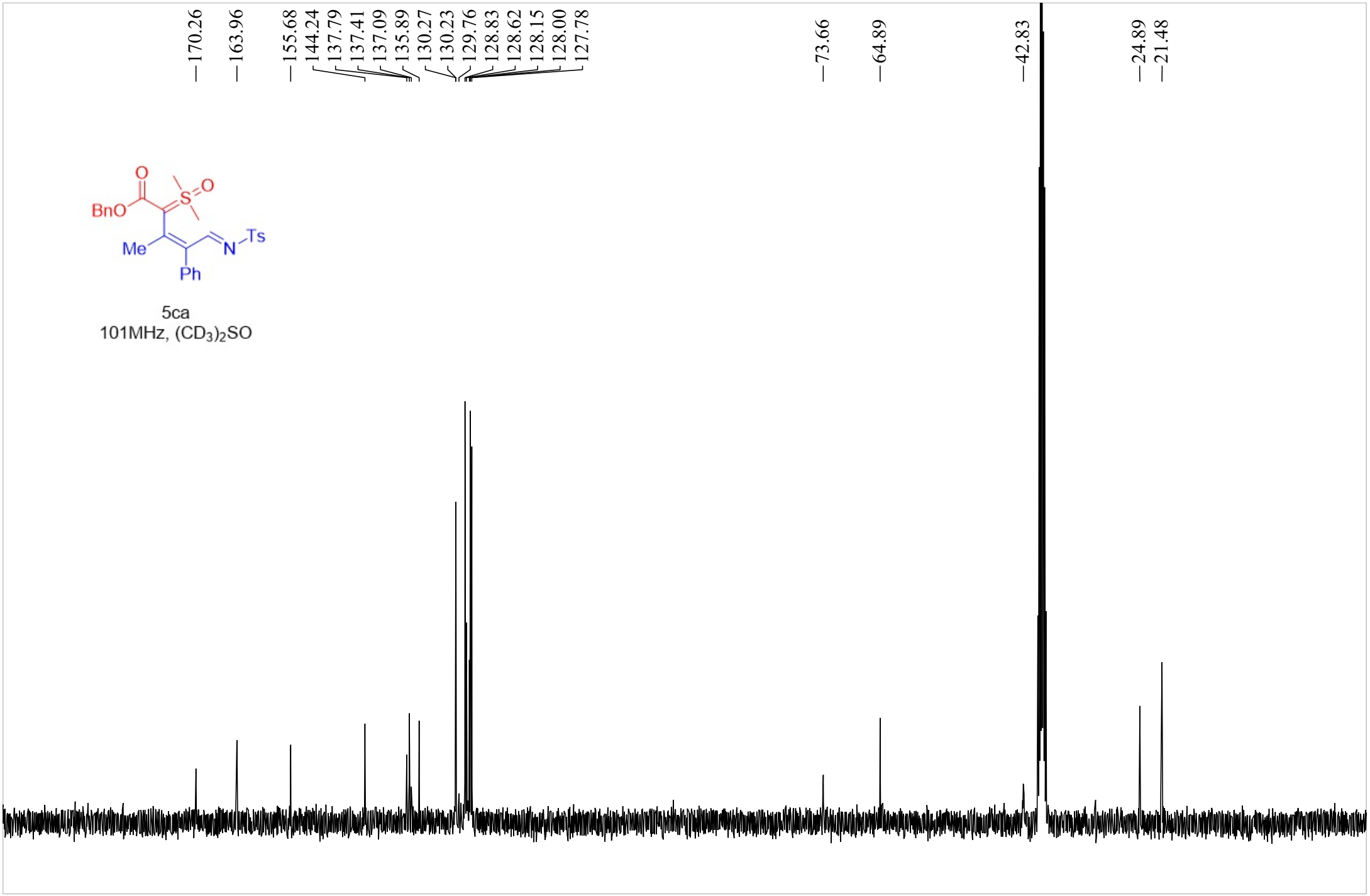
Z/E > 20:1
5af
400 MHz, $(CD_3)_2SO$

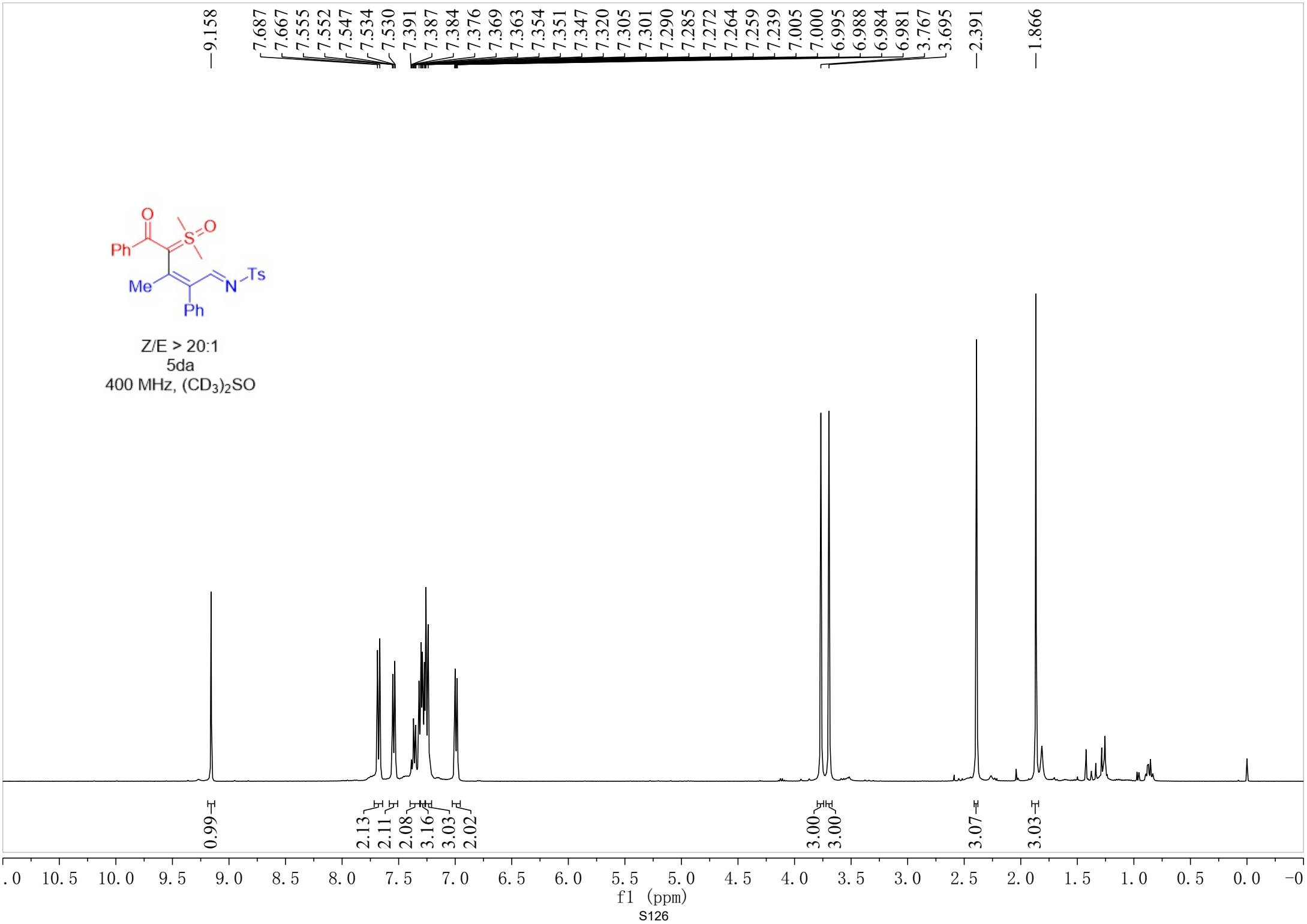

171.57
164.26
155.49
137.70
136.90
130.38
128.59
127.60
79.44
74.45
51.88
43.78
28.82
25.24
24.70
21.24
13.90
Me
Ph
5af
101 MHz, (CD3)2SO
f1 (ppm)

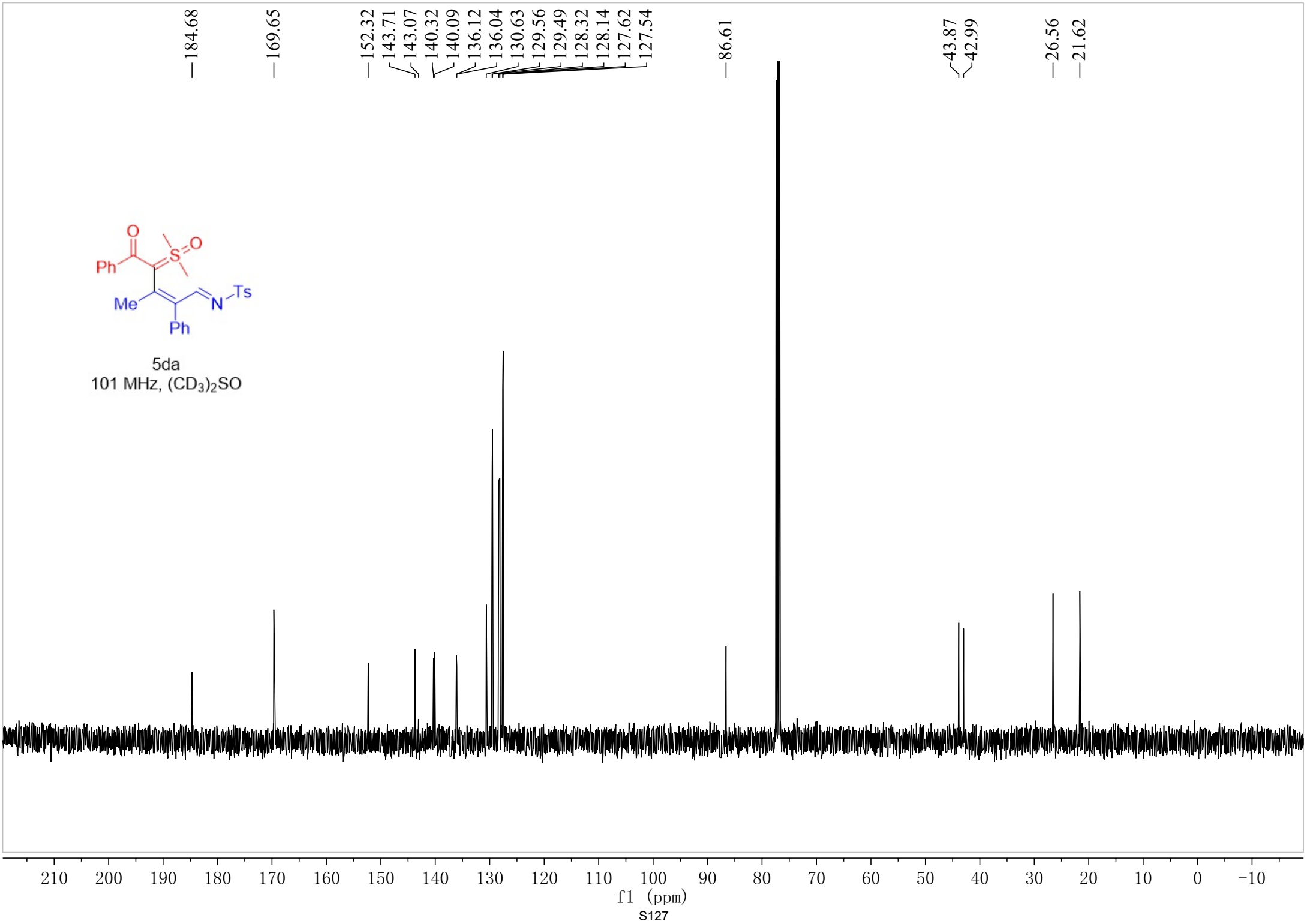

8.766
7.654
7.634
7.387
7.376
7.372
7.367
7.355
7.351
7.336
7.309
7.305
7.301
7.293
7.287
7.280
7.272
7.268
7.265
7.059
7.055
7.050
7.041
7.037
7.034
4.907
4.891
4.876
4.860
4.844
3.620
2.369
2.011
1.175
1.159
O
O
S
O
O
Me
N
Ts
Ph
Z/E > 20:1
5ba
400 MHz, (CD3)2SO
0.97
2.00
4.02
1.10
2.01
1.00
6.00
3.00
3.00
6.01
f1 (ppm)

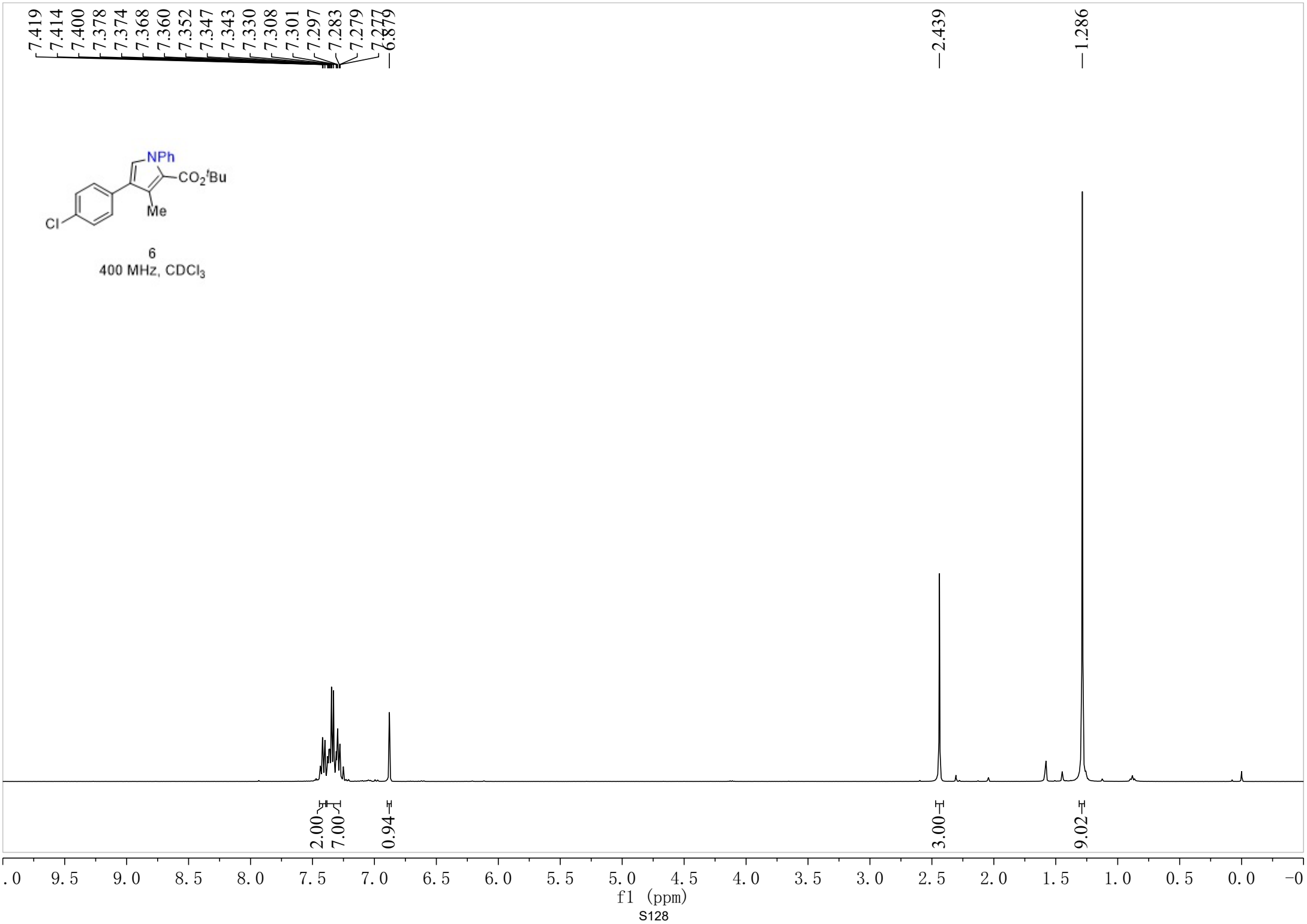

170.00
163.95
156.10
144.14
137.32
137.07
136.19
130.31
130.21
128.61
127.71
74.13
66.51
43.16
24.70
22.43
21.48
O
O
S
O
Me
N
Ts
5ba
101 MHz, (CD3)2CO
f1 (ppm)

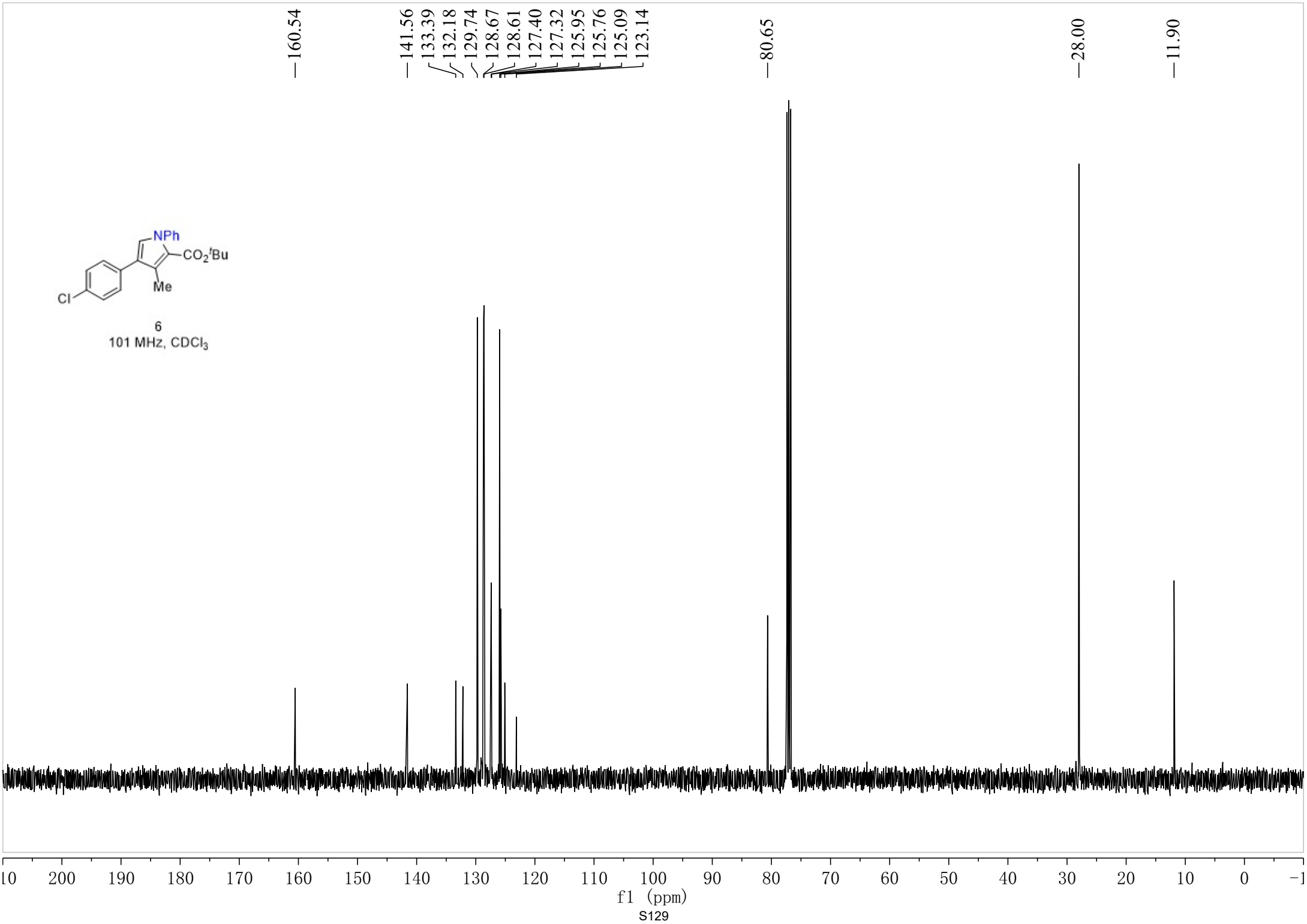

8.835
7.636
7.615
7.362
7.357
7.341
7.327
7.323
7.314
7.310
7.305
7.301
7.297
7.293
7.283
7.039
7.035
7.030
7.022
7.018
7.015
5.074
3.631
2.352
2.008
BnO
O
S
O
Me
N
Ts
Ph
Z/E > 20:1
5ca
400 MHz, (CD3)2SO
1.00
2.03
10.18
2.10
2.01
6.01
3.00
3.00
f1 (ppm)

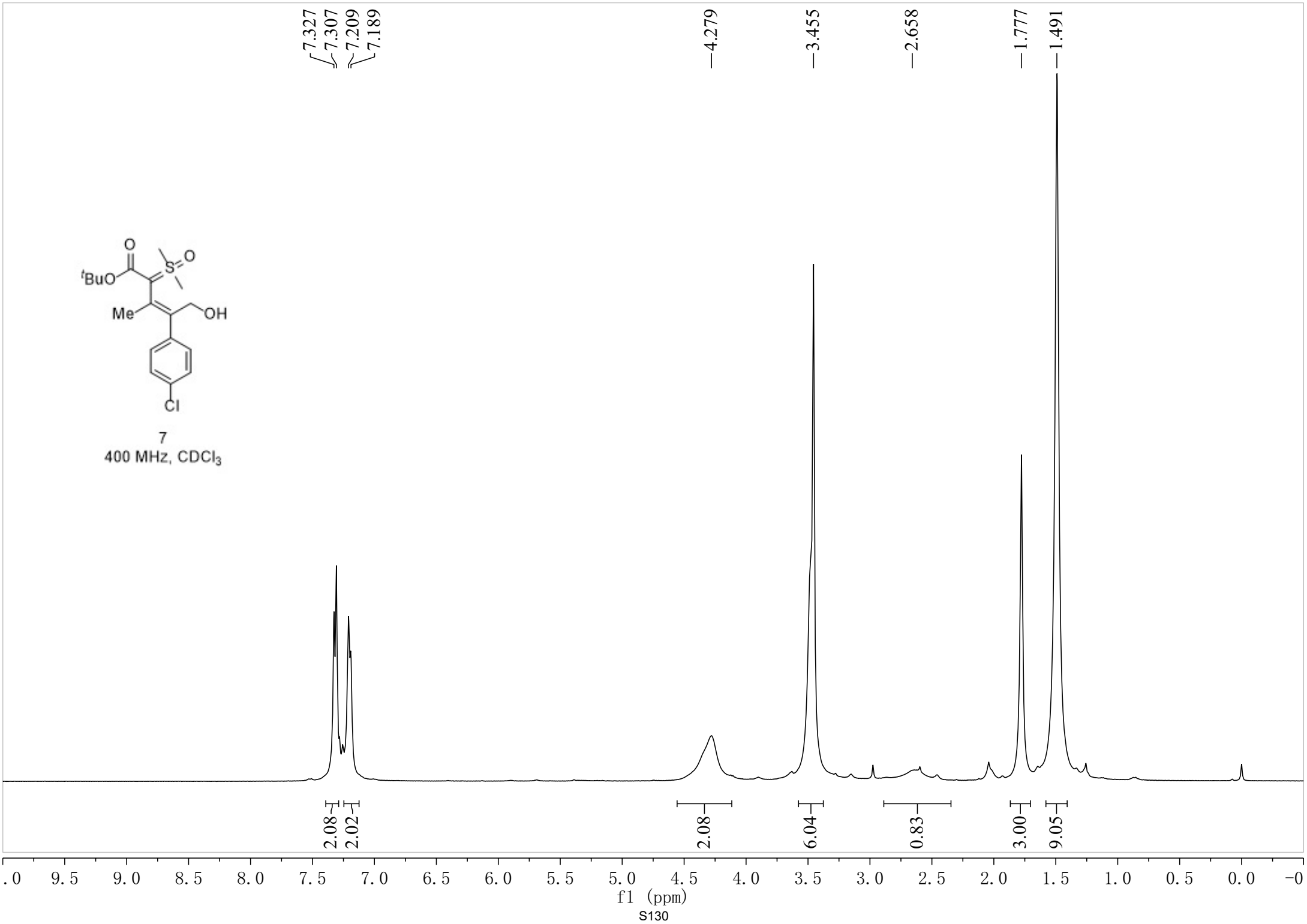

170.26
163.96
155.68
144.24
137.79
137.41
137.09
135.89
130.27
130.23
129.76
128.83
128.62
128.15
128.00
127.78
73.66
64.89
42.83
24.89
21.48
BnO
O
S
O
Me
N
Ts
Ph
5ca
101MHz, (CD3)2SO
f1 (ppm)

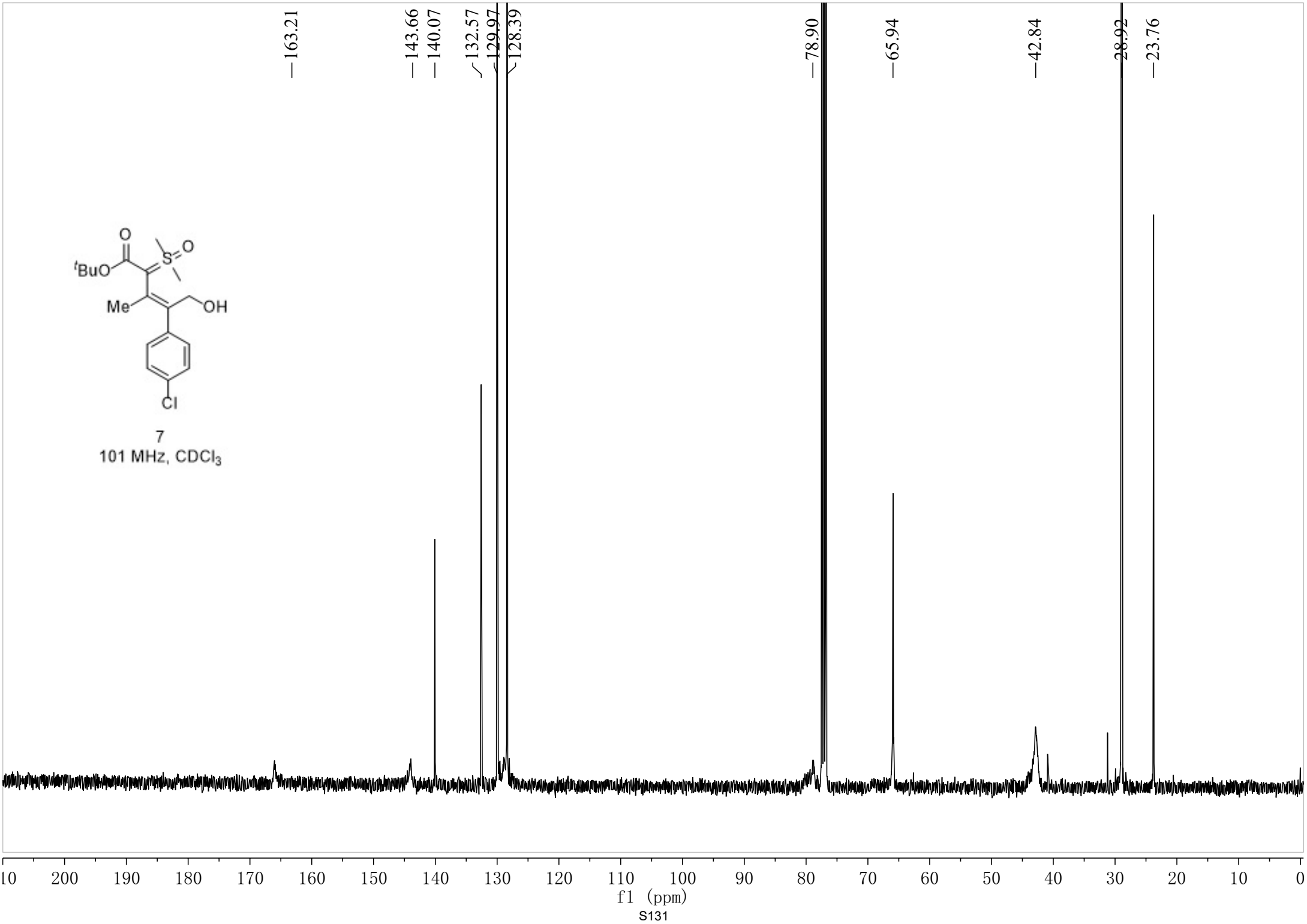

9.158
7.687
7.667
7.555
7.552
7.547
7.534
7.530
7.391
7.387
7.384
7.376
7.369
7.363
7.354
7.351
7.347
7.320
7.305
7.301
7.290
7.285
7.272
7.264
7.259
7.239
7.005
7.000
6.995
6.988
6.984
6.981
3.767
3.695
2.391
1.866
Ph
O
S
O
Me
Ph
N
Ts
Z/E > 20:1
5da
400 MHz, (CD3)2SO
0.99
2.13
2.11
2.08
3.16
3.03
2.02
3.00
3.00
3.07
3.03
f1 (ppm)

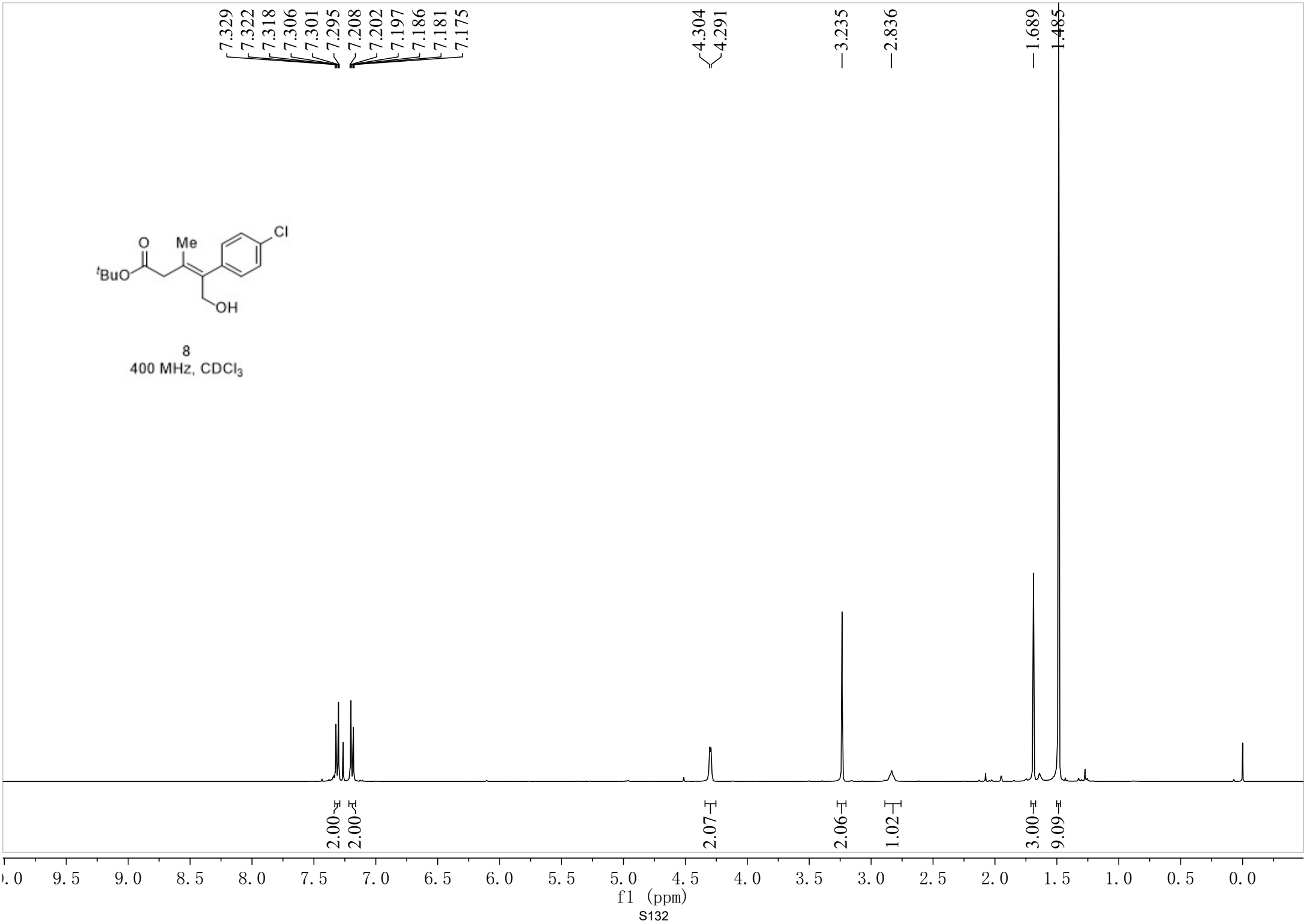

184.68
169.65
152.32
143.71
143.07
140.32
140.09
136.12
136.04
130.63
129.56
129.49
128.32
128.14
127.62
127.54
86.61
43.87
42.99
26.56
21.62
Ph
O
S
O
Me
N
Ts
Ph
5da
101 MHz, (CD3)2SO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

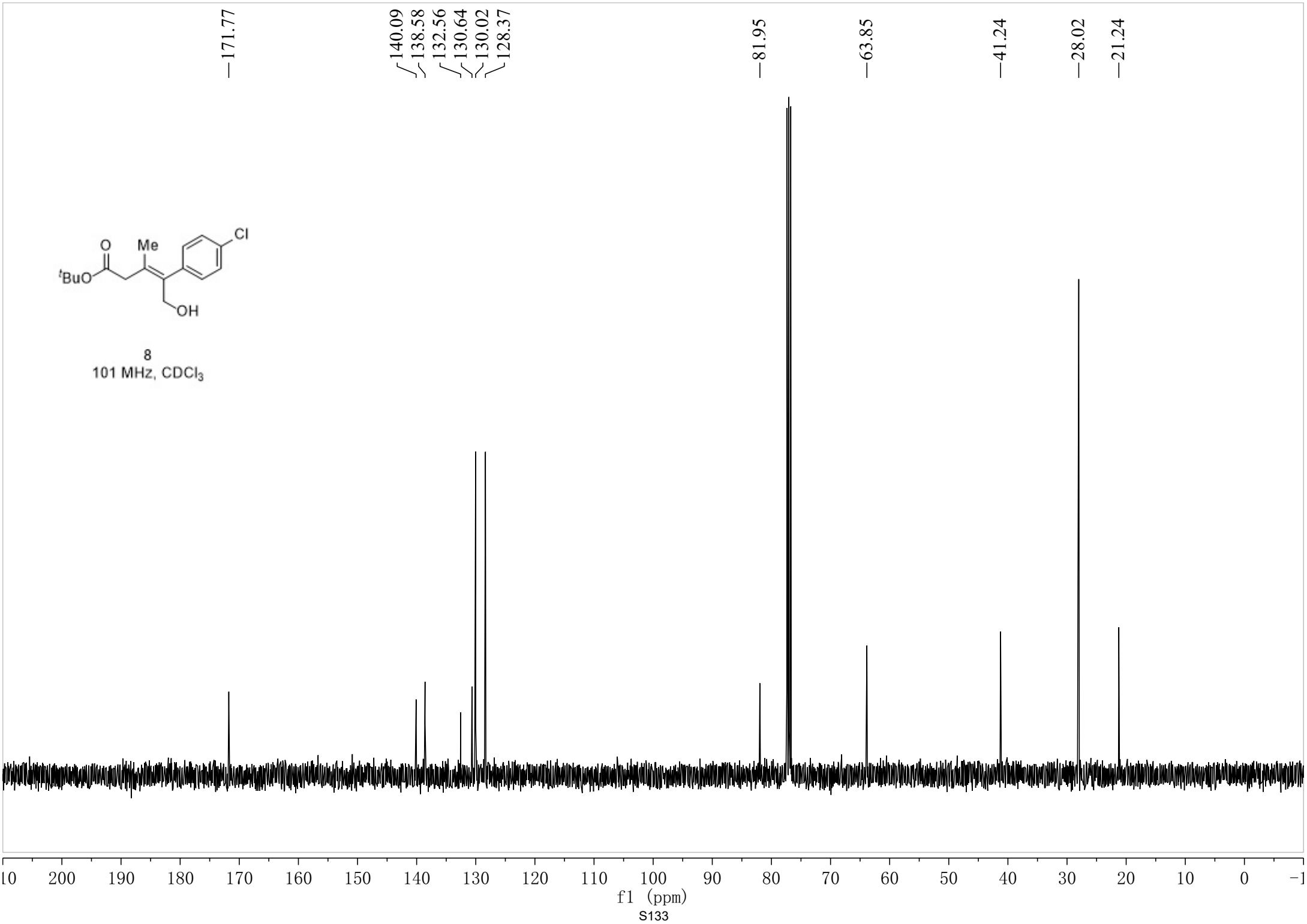

7.419
7.414
7.400
7.378
7.374
7.368
7.360
7.352
7.347
7.343
7.330
7.308
7.301
7.297
7.283
7.279
7.277
6.879
2.439
1.286
NPh
CO2tBu
Me
Cl
6
400 MHz, CDCl3
2.00
7.00
0.94
3.00
9.02
f1 (ppm)

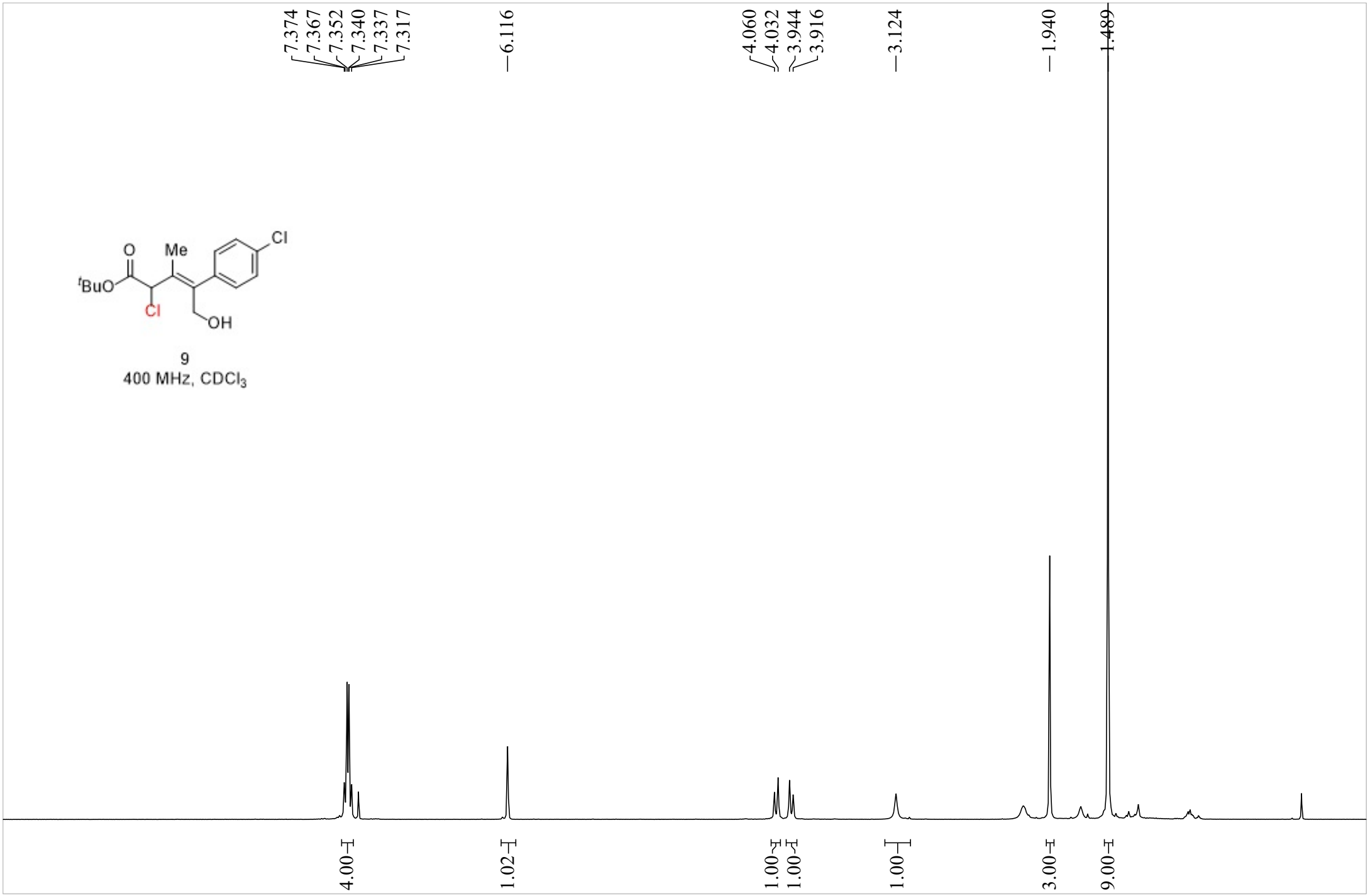

160.54
141.56
133.39
132.18
129.74
128.67
128.61
127.40
127.32
125.95
125.76
125.09
123.14
80.65
28.00
11.90
NPh
CO2tBu
Me
Cl
6
101 MHz, CDCl3
f1 (ppm)

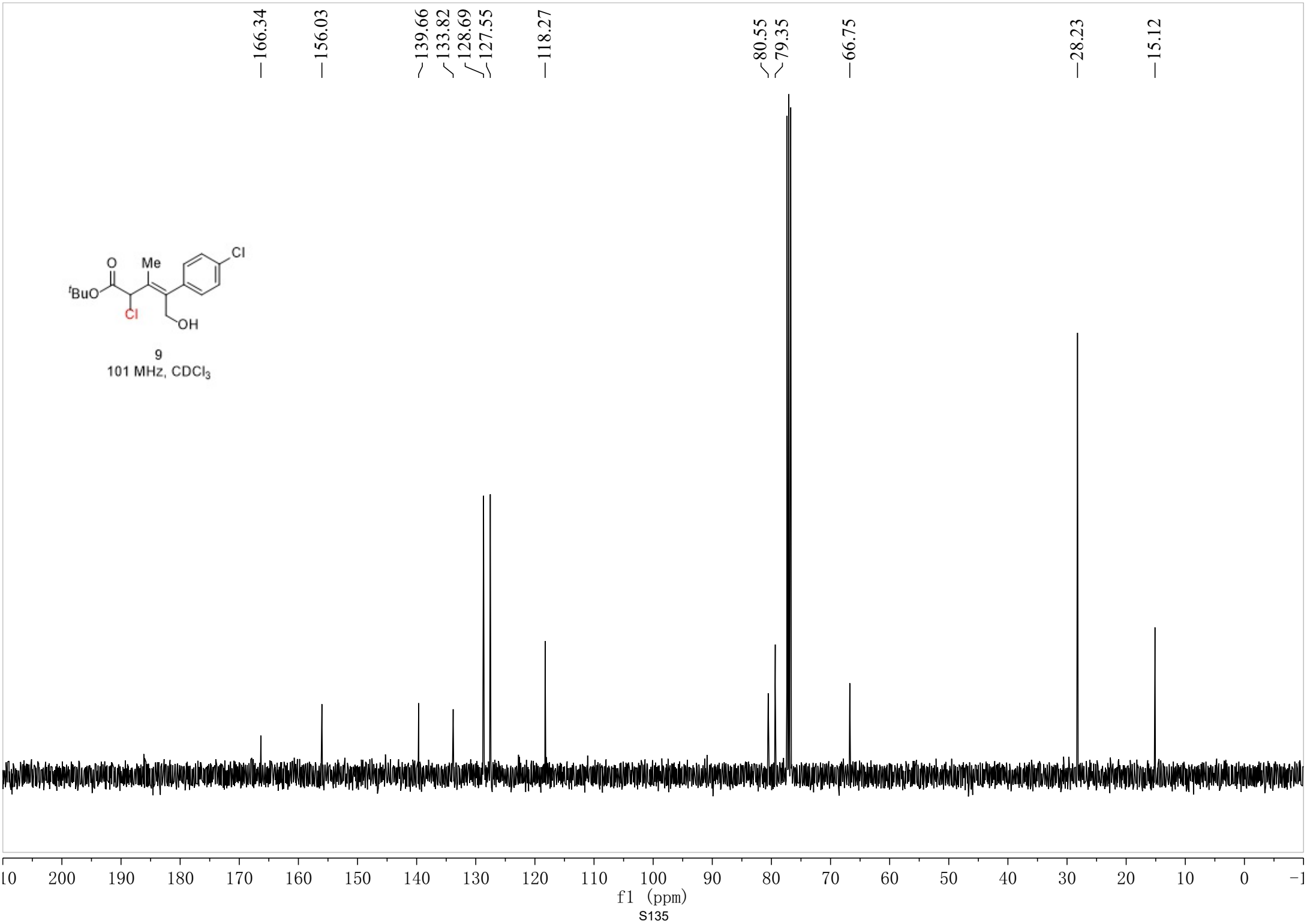

7.327
7.307
7.209
7.189
4.279
3.455
2.658
1.777
1.491
tBuO
O
S
O
Me
OH
Cl
7
400 MHz, CDCl3
2.08
2.02
2.08
6.04
0.83
3.00
9.05
f1 (ppm)

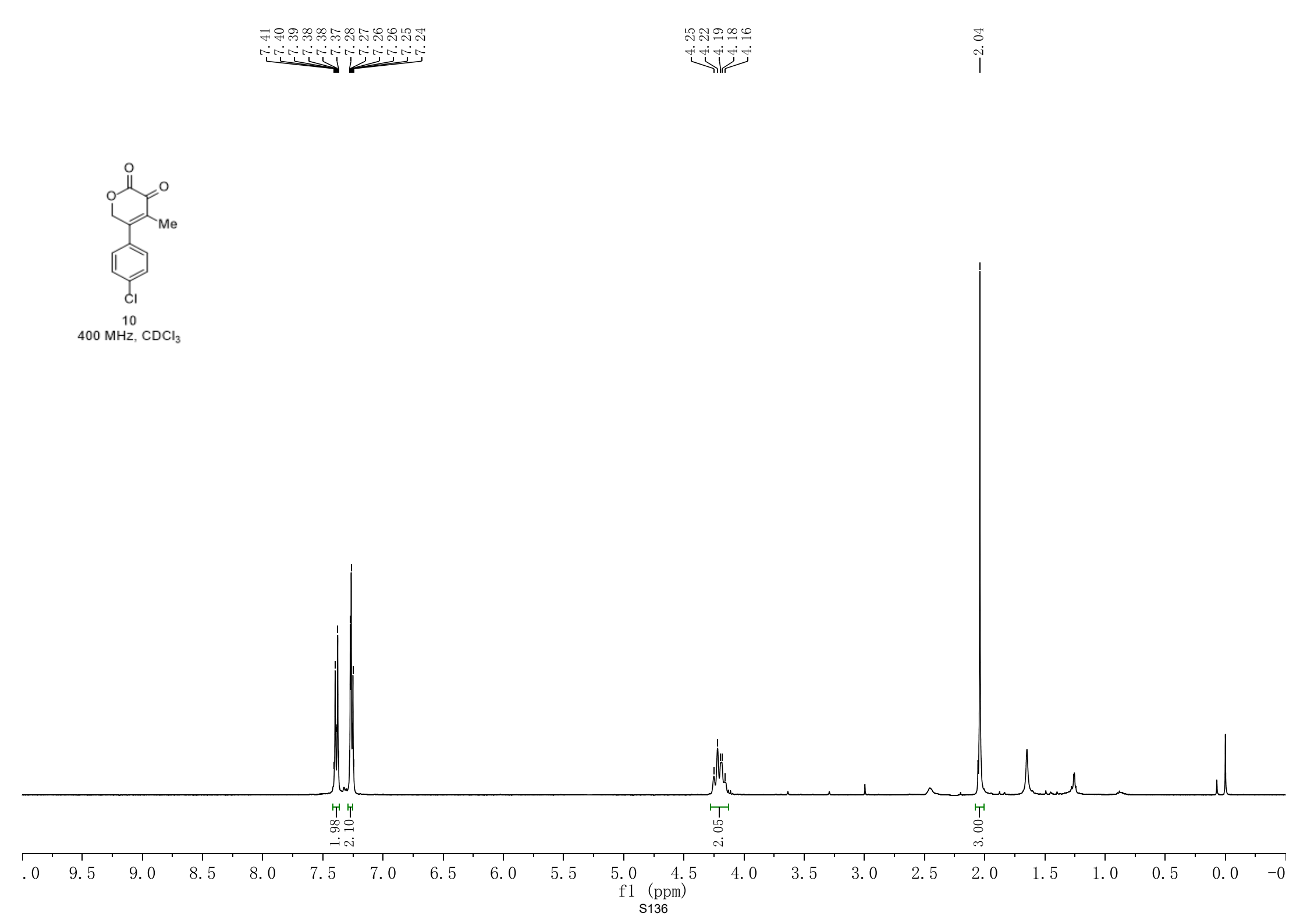

163.21
143.66
140.07
132.57
129.97
128.39
78.90
65.94
42.84
28.92
23.76
tBuO
O
S
O
Me
OH
Cl
7
101 MHz, CDCl3
f1 (ppm)

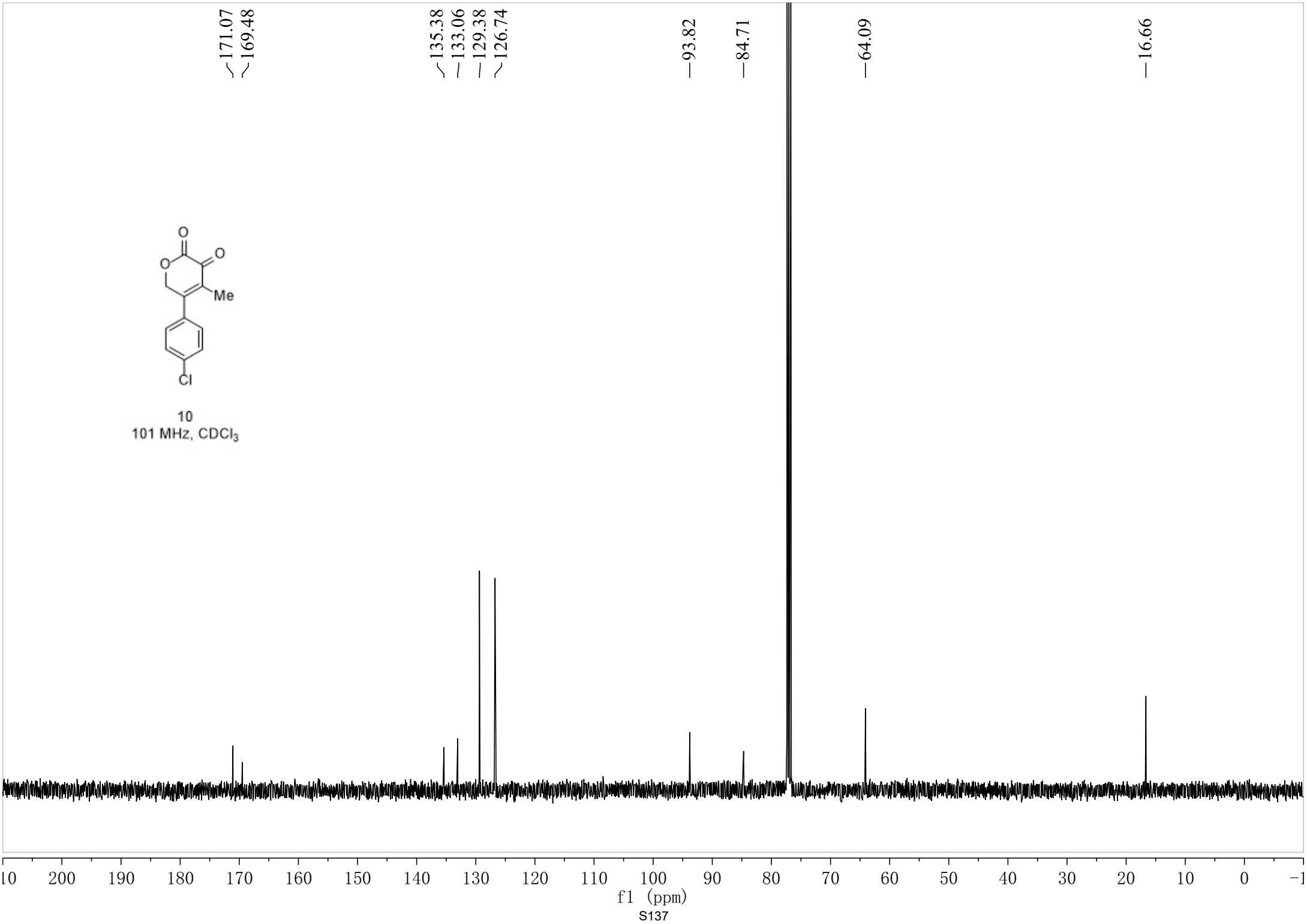

7.329
7.322
7.318
7.306
7.301
7.295
7.208
7.202
7.197
7.186
7.181
7.175
4.304
4.291
3.235
2.836
1.689
1.485
O
Me
Cl
tBuO
OH
8
400 MHz, CDCl3
2.00
2.00
2.07
2.06
1.02
3.00
9.09
f1 (ppm)

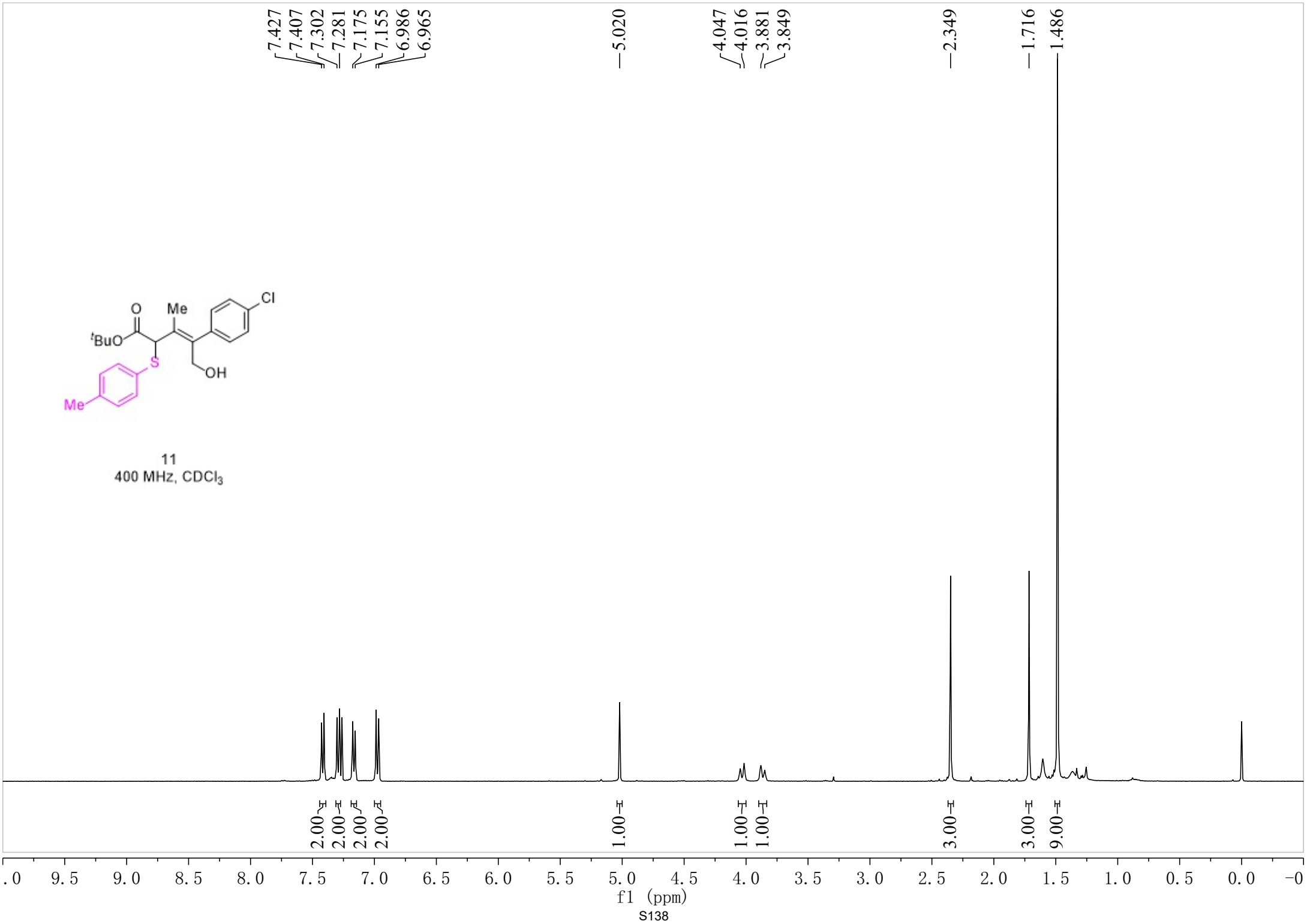

171.77
140.09
138.58
132.56
130.64
130.02
128.37
81.95
63.85
41.24
28.02
21.24
O
Me
Cl
tBuO
OH
8
101 MHz, CDCl3
f1 (ppm)

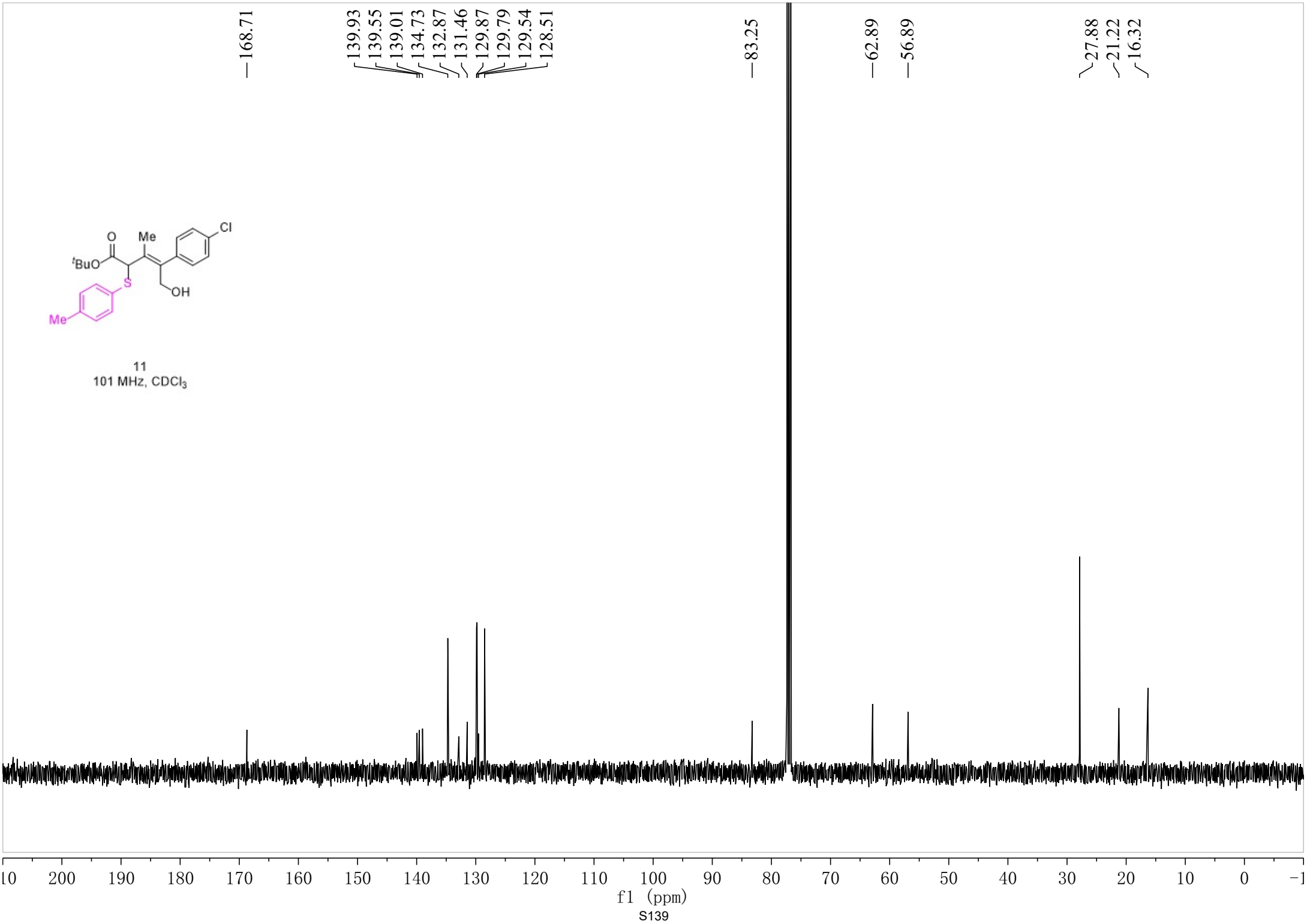

7.374
7.367
7.352
7.340
7.337
7.317
6.116
4.060
4.032
3.944
3.916
3.124
1.940
1.489
O
Me
Cl
tBuO
Cl
OH
9
400 MHz, CDCl3
4.00
1.02
1.00
1.00
1.00
3.00
9.00
f1 (ppm)

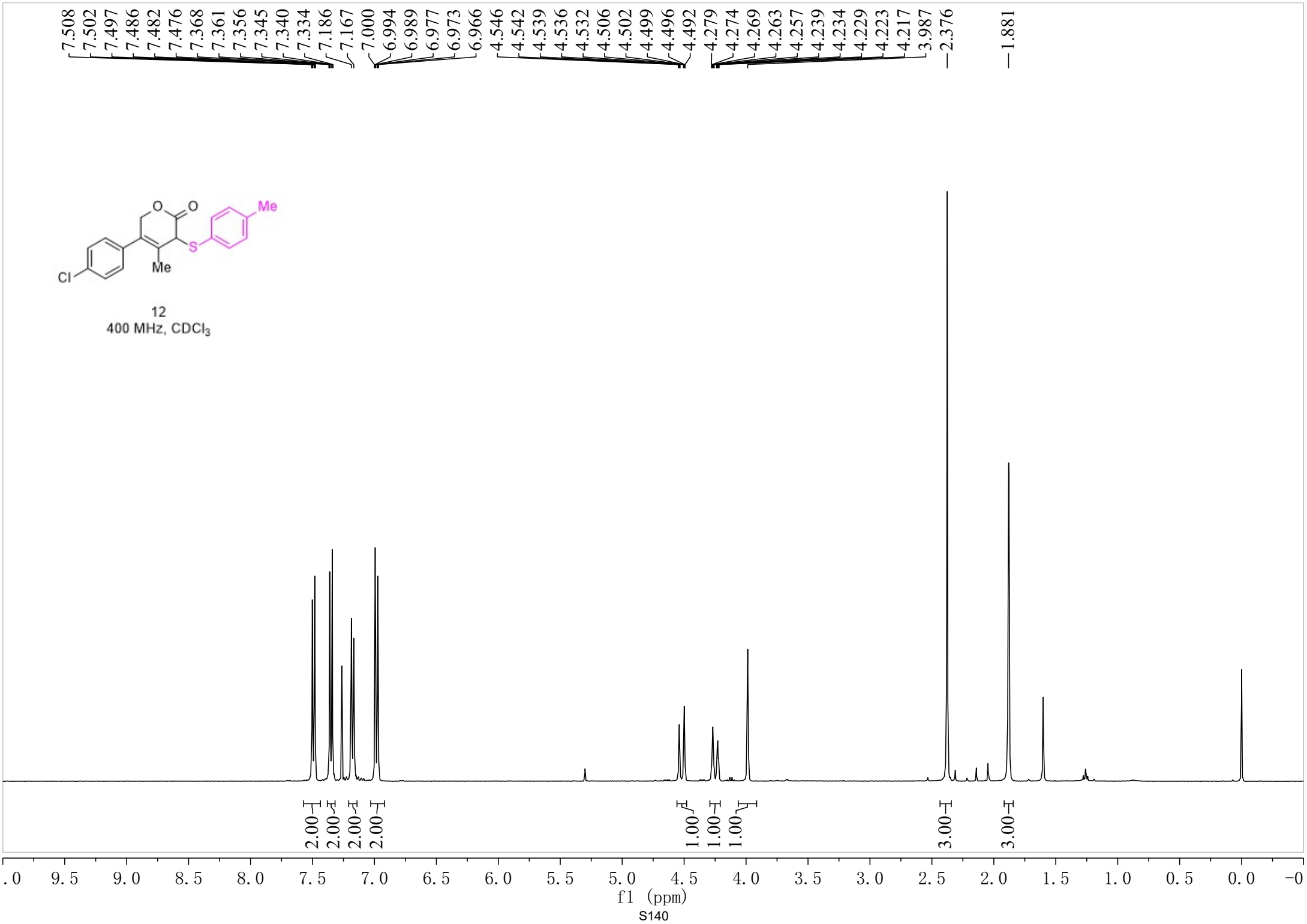

166.34
156.03
139.66
133.82
128.69
127.55
118.27
80.55
79.35
66.75
28.23
15.12
O
Me
Cl
tBuO
Cl
OH
9
101 MHz, CDCl3
f1 (ppm)

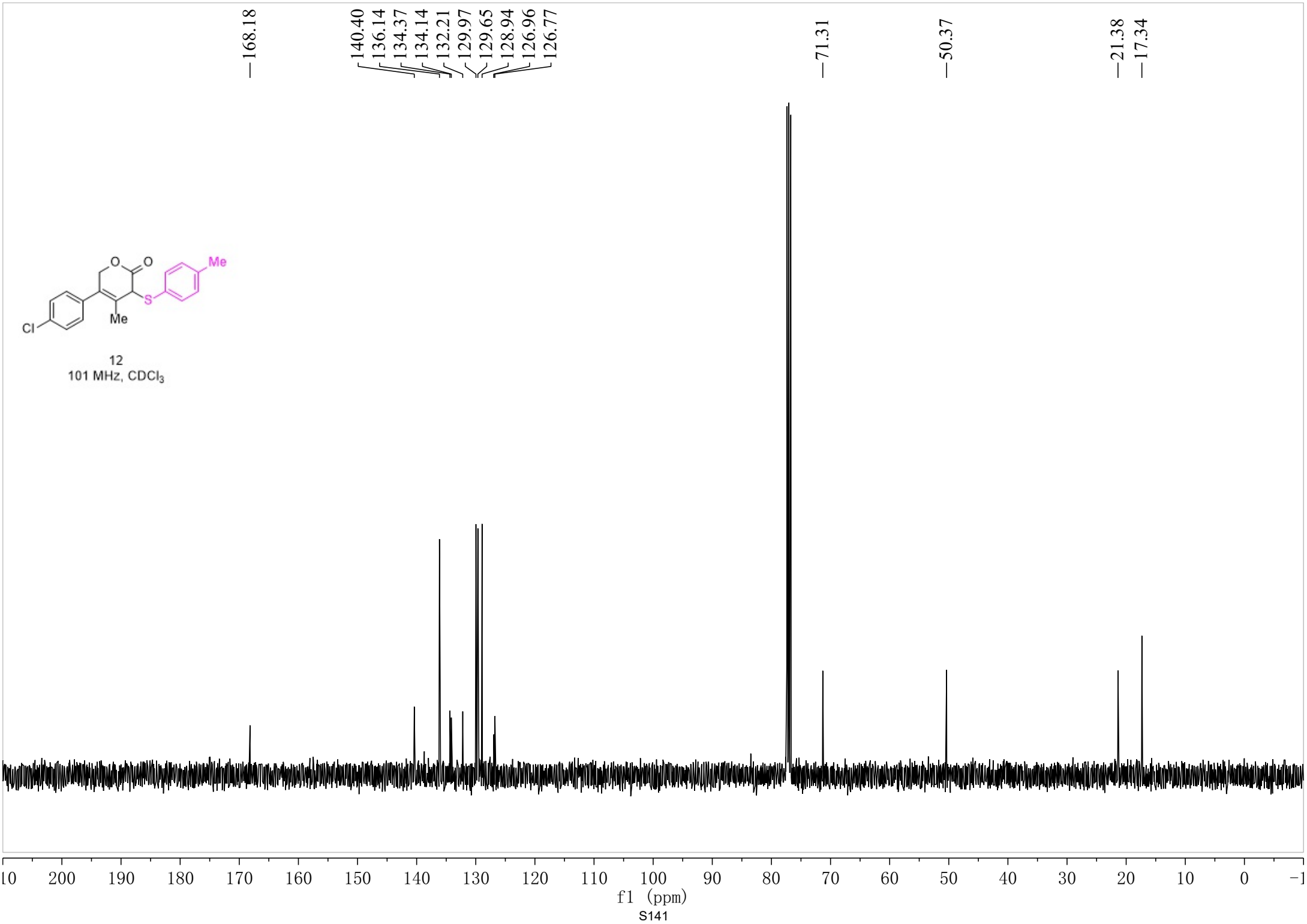

7.41
7.40
7.39
7.38
7.38
7.37
7.28
7.27
7.26
7.26
7.25
7.24
4.25
4.22
4.19
4.18
4.16
2.04
O
O
O
Me
Cl
10
400 MHz, CDCl3
1.98
2.10
2.05
3.00
f1 (ppm)


171.07
169.48
135.38
133.06
129.38
126.74
93.82
84.71
64.09
16.66
O
O
O
Me
Cl
10
101 MHz, CDCl3
f1 (ppm)


7.427
7.407
7.302
7.281
7.175
7.155
6.986
6.965
5.020
4.047
4.016
3.881
3.849
2.349
1.716
1.486
O
Me
Cl
tBuO
S
OH
Me
11
400 MHz, CDCl3
2.00
2.00
2.00
2.00
1.00
1.00
1.00
3.00
3.00
9.00
f1 (ppm)


168.71
139.93
139.55
139.01
134.73
132.87
131.46
129.87
129.79
129.54
128.51
83.25
62.89
56.89
27.88
21.22
16.32
O
Me
Cl
tBuO
S
OH
Me
11
101 MHz, CDCl3
f1 (ppm)


7.508
7.502
7.497
7.486
7.482
7.476
7.368
7.361
7.356
7.345
7.340
7.334
7.186
7.167
7.000
6.994
6.989
6.977
6.973
6.966
4.546
4.542
4.539
4.536
4.532
4.506
4.502
4.499
4.496
4.492
4.279
4.274
4.269
4.263
4.257
4.239
4.234
4.229
4.223
4.217
3.987
2.376
1.881
O
O
Me
S
Me
Cl
12
400 MHz, CDCl3
2.00
2.00
2.00
2.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)


168.18
140.40
136.14
134.37
134.14
132.21
129.97
129.65
128.94
126.96
126.77
71.31
50.37
21.38
17.34
O
O
Me
S
Me
Cl
12
101 MHz, CDCl3
f1 (ppm)